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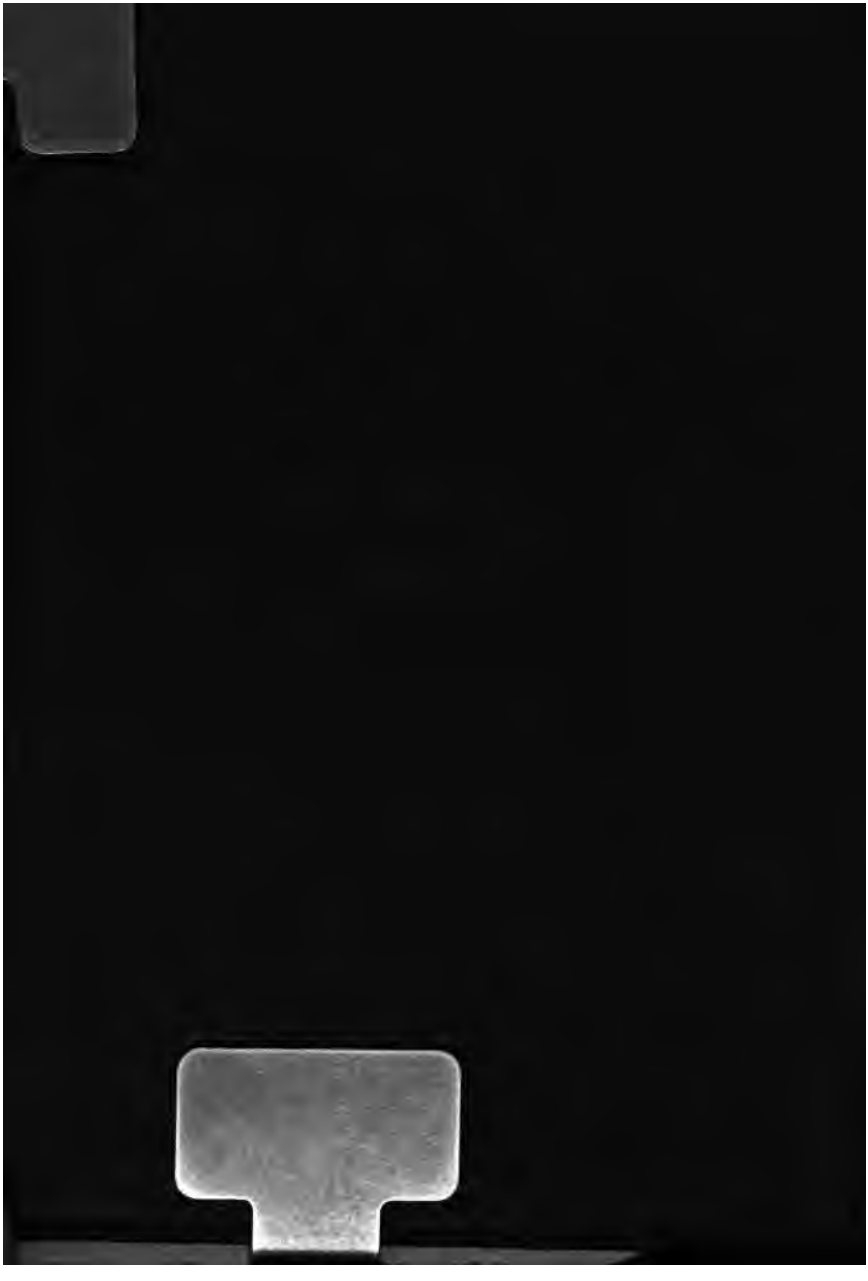

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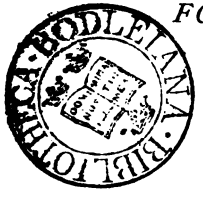


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Oxford

AT THE CLARENDON PRESS

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# PREFACE.

THIS little book is intended to supply to Students of Chemistry an outline of the most interesting and useful facts pertaining to the Science, and of the most important ideas which have been got from a study of those facts.

The method of exposition differs from that which is adopted in most other treatises of Chemistry; for I describe and compare individual facts, so as to lead the mind of the reader towards general principles, instead of stating the general principles first and then proceeding to illustrate them by details.

The book is intended for the use of beginners in Chemistry, and also of Students who, having made some progress in the Science, wish to have an outline of the chief facts and theories of mineral and of organic Chemistry. Those who wish to proceed further and to obtain full particulars of any one part of the subject, will need to consult such books as Gmelin's Handbook, Watts's Dictionary, Miller's Elements, Gerhardt's Traité de Chimie organique, or Kekulé's admirable Lehrbuch der organischen Chemie. It is not intended as a substitute for *vivâ voce* and experimental teaching, but rather as a guide and aid to Students and Teachers. A judicious Teacher will amplify the brief explanations and descriptions which I give; and

will shew experimentally the reactions and transformations which I mention. A Learner who wants to recal to mind what he has seen and heard may refer to the book for the substance of it.

The absolute "volume" which I have for many years adopted in my classes is here employed in the calculations relating to gases. The knowledge of this absolute volume is of value to Learners because it leads them easily from a class of similar facts to an important general conclusion, and it supplies to Chemists a ready means of calculating the weight of any given measure of gas or vapour. This absolute volume is in round numbers 11.2 litres, which is the bulk of one gramme of hydrogen, of sixteen grammes of oxygen, of fourteen grammes of nitrogen, &c., at the normal temperature and pressure; in fact the bulk of that quantity of any one of those gases which weighs as many grammes as there are units in the number expressing its atomic weight. Students will do well to work out the answers to the questions appended to the first few chapters, and thereby to practise themselves in using the elementary facts of Chemistry. I propose to publish answers to the questions shortly.

A. W. WILLIAMSON.

UNIVERSITY COLLEGE, LONDON,
*October* 1865.

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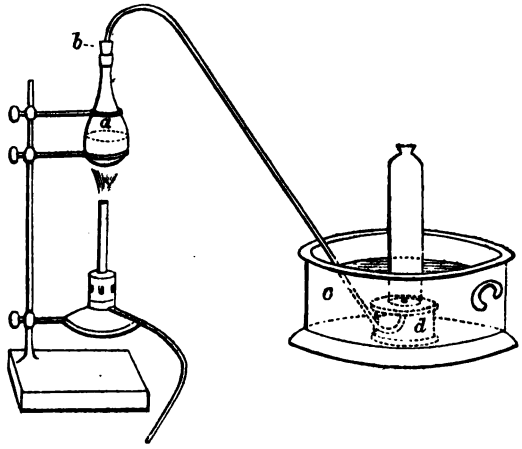
# CHAPTER I.

1. **Oxygen** ($O^2$, $O = 16$) is most conveniently prepared by heating pure potassic chlorate (chlorate of potash) in a glass flask or tube. The salt first melts and then appears to boil, the bubbles which come off from it, being oxygen, are col-




Preparation of Oxygen.—*a* Florence flask, containing chlorate; *b* perforated cork; *c* bent tube; *d* bee-hive.

lected by displacement of water in a glass jar inverted in a pneumatic trough. The gas should be tested from time to time as it comes off, by plunging into it the glowing end of a

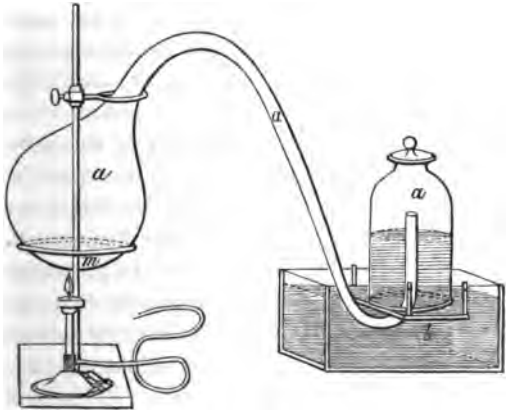
splint of wood. If the splint burst sharply into flame the gas may be assumed to be pure enough for most purposes. But if the purest obtainable oxygen be required, the operator ought to select a flask only just large enough to contain the quantity of chlorate which he wishes to decompose, and he ought not only to reject those portions of gas which are first driven out of the flask and which do not make the glowing splint burst sharply into flame, but he ought before collecting his gas to allow the process to continue for some time longer, so that the air may be completely swept out of the flask by the oxygen. The pure oxygen which then comes should be collected over mercury, as by passing through water it would get contaminated by nitrogen which was dissolved in the water. Pure oxygen is completely absorbed by a solution of pyrogallic acid in strong potash, and whatever remains undissolved by this re-agent (excepting a trace of carbonic oxide) must be some other gas which had been mixed with the oxygen. Some persons recommend the addition of a little manganic peroxide to the chlorate which is to be heated, but although the chlorate is thus more rapidly decomposed, the advantage is dearly purchased, for the gas set free is liable to contain chlorine.

Potassic chlorate if completely decomposed by heat, yields 39.183 per cent. of its weight of oxygen gas, the remaining salt being potassic chloride, a compound of potassium with chlorine. Some of the chlorate employed is however usually carried away by the oxygen in the form of spray and thus escapes decomposition; and some oxygen is often retained in the form of potassic per-chlorate, a salt which requires for its decomposition a higher temperature than that at which the chlorate is decomposed.

When oxygen is wanted in very large quantities, it is more economically prepared by heating a mineral called "Man-

ganese." The process is performed in a stone-ware retort similar to those used for making coal gas. The mineral consists of the metal manganese combined with oxygen, but the utmost heat is unable to drive off more than one-third of the oxygen contained in the pure mineral.

**2.** Oxygen is a component of atmospheric air, and can be prepared from it in a pure state. An experiment of Lavoisier's shews this result in a very interesting form. Mercury is boiled in a convenient vessel containing say 100 cubic centimeters of air, care being taken that no air shall escape. At the end of twelve days, a red powder is formed by combination of some of the mercury with oxygen, and if




Preparation of Oxygen from Air.—*a a a* Globe, &c., containing metallic mercury and air ; *b* pneumatic trough.

a burning taper be plunged into the residual gas the taper goes out. While losing its oxygen the air has lost the power of supporting combustion. If the red compound of mercury and oxygen be heated to a temperature sufficiently above that at which it was formed, it is decomposed into metallic

mercury and oxygen, and if this oxygen be returned to the air from which it had been removed by the action of mercury, it restores to the air the power of supporting combustion.

3. Iron wire can be lighted in an atmosphere of oxygen, by fixing a piece of tinder to its end, and kindling it before it is put into the gas. The iron burns with great intensity, and white hot globules are formed at the end of the wire, and increase in size till they drop off. These globules consist of iron combined with oxygen.

Phosphorus also burns in oxygen with great intensity. A small piece of that substance ought to be carefully dried, and put into a little copper spoon. It can very easily be lighted by a match while still surrounded by air, and if then lowered into a jar of oxygen it immediately burns with far greater brilliancy and rapidity than in air, and gives off a dazzling light. A white powder called phosphoric acid is formed in this process, by combination of the phosphorus and oxygen. When sulphur is burned in oxygen there is no solid or visible product formed, and the blue flame which is produced during the process is far less luminous than the white flame of the burning phosphorus. In proportion however as the combustion proceeds the oxygen disappears, and in its place is found a gas of an exceedingly powerful and well-known smell. This gas, called sulphurous acid, is a compound of sulphur and oxygen.

The combustion of charcoal affords another interesting instance of combination with oxygen. A piece of light wood charcoal should be selected for the purpose, and in proportion as it burns away, a gas is produced containing carbon combined with oxygen, and possessing feebly acid properties. This gas (called carbonic acid) is readily absorbed by caustic potash, and can thus be separated from oxygen.

**4.** In all these processes of combustion there are products formed which weigh exactly as much as the materials used in their formation; and in no case of combustion is there a destruction of materials. Every kilogramme of sulphur which is burnt takes up a kilogramme of oxygen, forming two kilogrammes of sulphurous acid, and if this sulphurous acid were collected, the sulphur could be recovered from it. In like manner every kilogramme of carbon fully burnt forms $3\frac{2}{3}$ kilogrammes of carbonic acid, by combining with $2\frac{2}{3}$ kilogrammes of oxygen, and both the carbon and oxygen can be got out of this compound by suitable processes.

But except in the one particular of weight, these products have different properties from their materials; and it is the business of chemistry to explain the changes of property which substances undergo by combining with one another.

**5.** Oxygen is a colourless gas devoid of taste and smell. It is a little heavier than atmospheric air. It is 16 times as heavy as hydrogen at the same temperature and pressure, and is accordingly described as having a density equal to 16, when that of hydrogen is represented by unity.

In the metrical system, which is the most convenient for calculations, the volume of a fixed weight of oxygen is thus stated: 16 grammes of oxygen measure 11.19 or very nearly 11.2 litres at 0°C, and 760 millimeters of mercury pressure. The same measure (11.2 litres) of water weighs nearly 700 times as much; so that under these conditions of temperature and pressure oxygen has about $\frac{1}{700}$ the density (or specific gravity) of water. In grains and cubic inches the same fact may be thus stated: 16 grains of oxygen at 0°C and 29.9 inches pressure measure 44.473 cubic inches. When 100 measures of oxygen are measured off at 0°C and then heated to 1°C they become 100.3665. When heated to 2°C they

become 100.7330 and so on, gaining .3665 for every degree rise of temperature counted from 0°C. It follows from this, that if 100 volumes of the gas were measured off at 15°C, and then heated to 16°C, the increase of volume would be found by the following proportion:

$$100+15\times.3665 : 100+16\times.3665 = 100 : x,$$

or $105.4975 : 105.8640 = 100 : x$, which gives us for the volume at 16°C, $x=100.34$.

**6.** If oxygen were kept at the same temperature and subjected to greater and greater pressure it would diminish in volume in proportion to the increase of pressure. Thus if a litre of oxygen were measured off in stormy weather while the barometer stood at 700 millimeters, and then put aside and measured at the same temperature, but after the barometer had risen to a height of 750 millimeters, it would be found to have diminished in volume in the proportion of 75 to 70, and would only measure 0.933 of a litre. It is convenient to state this law thus: the density of oxygen at a given temperature is proportional to the pressure to which it is subjected. By exposure to a pressure of about 300 atmospheres, oxygen has been reduced to $\frac{1}{300}$ of its ordinary volume, but further pressure did not appear to produce a corresponding diminution of volume.

When oxygen is heated and yet not allowed to expand, it presses against the sides of the vessel in which it is contained with an amount of force which increases, with rise of temperature, in the same proportion in which expansion takes place under constant pressure. Thus if we measure out 1 litre of oxygen at the temperature of 0°C, and if while heating the gas to 15°C, we wish to prevent it from expanding, we must increase the pressure upon it in round numbers in the proportion of 273 to 273 + 15. If at the commencement of the experiment a barometer in the same room stood at a height of 760 millimeters, the litre of

oxygen was under a pressure of the air equal to a column of mercury 760 millimeters (or 30 inches) high; and the pressure required to prevent the air from expanding whilst it is being heated is found by the proportion: $273 : 288 = 760 : x$ which gives us $x = 801.7$; so that we must increase the atmospheric pressure by an amount equal to a column of mercury rather more than 41 millimeters high to keep our oxygen to the bulk of a litre when it is heated from 0°C to 15°C.

**7.** Oxygen is absorbed by venous blood, and imparts to it a bright red colour. Carbonic acid is given off at the same time that the oxygen is absorbed. The respiration of animals takes place quite freely in oxygen, but the pure gas has too stimulating an action, and soon disturbs the regular working of the process, by inducing too rapid an oxidation for the requirements of the system.

Fresh leaves of plants give off oxygen, when placed in the sunshine, in contact with carbonic acid.

**8. Ozone.** Under particular conditions, the oxygen which is given off in the decomposition of dilute sulphuric acid by the galvanic battery, is found to have a sickly smell, owing to the presence in it of a substance of more actively oxidizing properties than ordinary oxygen. The same substance is said to be formed by the action of an electrical brush discharge on pure oxygen. It is destroyed by passing the oxygen containing it through a glass tube heated to redness by a lamp; and by contact with india-rubber, or cork, or any other vegetable or animal substance, it is immediately destroyed, producing water and carbonic acid by the oxidation of the hydrogen and carbon of the vegetable substance. Even metallic silver is transformed into an oxide by contact with this powerful substance.

Until the substance is isolated and fully examined, we cannot with certainty pronounce upon its nature, but some

chemists are of opinion that it is nothing else than oxygen which has undergone a change of properties.

The very great majority of the compounds of oxygen hold that substance so firmly that it cannot support combustion so easily as in the free state; but there are some compounds of oxygen in which it has more active combining tendencies than in the free state, and some of them are known to produce effects similar to those by which ozone is usually tested. The atmosphere is said by some persons to contain ozone, when paper moistened with potassic iodide and starch turns blue by contact with it.

## APPENDIX TO CHAPTER I.

### PROBLEMS.

1. What weight of oxygen is contained in one kilogramme of potassic chlorate?

2. 100 litres of oxygen at 0°C, and 0.760 millimeters barometric pressure, are wanted. How much potassic chlorate must be decomposed for its production, assuming that all the oxygen can be expelled from the salt?

3. 30 litres of oxygen were measured off at 15°C. What would be the volume of the gas at 0°C, the pressure remaining unchanged?

4. What weight of oxygen is required to fill a globe of 13 litres capacity, at the temperature of 12°C?

5. 10 litres of oxygen are measured off at 14°F. Required the volume of the gas at 15°C.

6. 230 cubic centimeters of oxygen are measured off at 14°C and 740 millimeters mercurial pressure. Required the volume of the gas at the normal temperature and pressure (0°C and 760 millimeters).

7. 43 grammes of oxygen were measured off at the normal pressure, and at a temperature such that their density was 18.

Required the volume of the gas in litres, and the temperature at which it was measured.

8. A flask is filled with oxygen at 0°C, at 760 mm. pressure, and the flask is then tightly corked. The flask would burst if exposed to an outward pressure of 1500 mm. At what temperature would the oxygen exert this pressure, assuming the volume of the flask to remain the same as when cold?

9. A litre of oxygen is confined in a glass flask at 10°C by the atmospheric pressure, added to that of a column of mercury 60 millimeters high. The flask must be heated to 300°C, without any increase of volume taking place in the oxygen. How high must the column of mercury then be which presses on the gas, should the atmospheric pressure remain unchanged?

10. A litre of oxygen is required of the density of 100. What weight of potassic chlorate must be used for its liberation, and what total pressure must be applied to it?

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# CHAPTER II.

**9. Hydrogen** ($H^2$, $H=1$) is most conveniently prepared by pouring onto metallic zinc some sulphuric acid previously mixed with three or four times its volume of water. The gas comes off from the surface of the zinc and can be collected in the same way as oxygen. The process by which it is here given off is illustrative of the chemical nature of hydrogen, for the so-called sulphuric acid consists of hydrogen combined with sulphur and oxygen, and the metal zinc actually pushes the hydrogen out of this compound and takes its place. It will be seen that there are many other cases of a metal combining with the same elements as hydrogen. If a sufficient quantity of zinc be used to expel all the

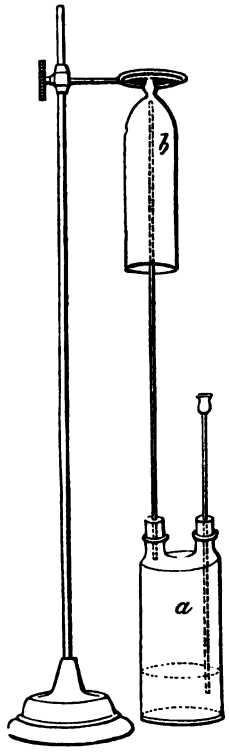
hydrogen from the sulphuric acid employed in the experiment, it will be found that the liquid left in the bottle consists of a solution of a compound of zinc with sulphur and oxygen, called zinc sulphate. This salt can be obtained in the form of beautiful white crystals, by carefully evaporating off the water until the solution, on cooling, deposits some of the substance dissolved in it. Iron wire also dissolves in dilute sulphuric acid giving off hydrogen gas, and forming a crystallizable salt, called ferrous sulphate, consisting of iron combined with sulphur and oxygen. But the hydrogen prepared by the use of iron, usually has an unpleasant smell, owing to the presence in it of a compound of carbon and hydrogen. Sulphur, phosphorus, and arsenic are not uncommon impurities in hydrogen, and the vapour of water necessarily accompanies it from the generating flask.

**10.** To remove these impurities the gas should be passed slowly through a tube containing pieces of pumice-stone moistened with a solution of argentic nitrate, which keeps back the sulphuretted hydrogen, phosphuretted hydrogen, and arseniuretted hydrogen; and through a second tube containing pumice moistened with strong oil of vitriol, which absorbs the moisture in the gas.

Many metals are capable of decomposing water and liberating hydrogen from it, just as zinc and iron decompose sulphuric acid; but some of these metals, such as potassium and sodium, are too expensive to be used in competition with either of the above processes; and others, such as iron, only decompose water at high temperatures, which it is not always convenient to employ.

**11.** Hydrogen, when collected free from air, does not explode, but burns quietly when ignited. Mere traces of oxygen can be discovered in it by a diminution of the volume of the gas when left in contact with potassic pyrogallate over mercury.

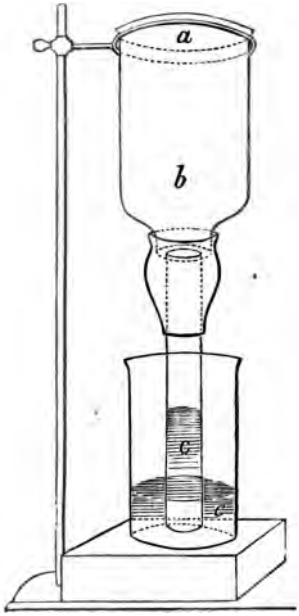
Hydrogen is the lightest substance known, one gramme of it measures exactly as much as 16 grammes of oxygen, viz. 11.19 litres, so that oxygen is 16 times as heavy as hydrogen. One grain of hydrogen at 0°C and 760 millimeters pressure measures 44.473 cubic inches. Hydrogen has less than $\frac{1}{14}$ the density of air ($\frac{1}{14.45}$), and it accordingly tends to rise to the top of any vessel containing air. Thus a glass bell-jar suspended with its mouth downwards, may be filled with hydrogen, by leading a rapid current of the gas up to the top of the bell-jar, by a tube, as shewn in the annexed figure. That the hydrogen remains for a short time in the bell-jar can be proved by passing a lighted taper up it, when the taper is extinguished but sets fire to the hydrogen. Its extreme lightness makes this gas particularly suitable for filling balloons.




Collection of Hydrogen by displacement of Air. — *a* Tubulated bottle for evolving gas; *b* inverted bell-jar.

Hydrogen is a very bad conductor of sound, as it is easy to prove by agitating a small bell in a jar full of the gas, and then agitating it in a similar jar full of air.

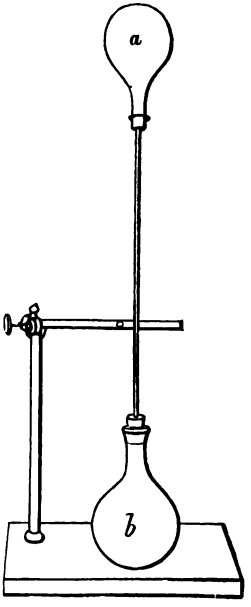
**12.** It is the most difficult gas to keep, for its particles are so exceedingly light and mobile that they find their way out through any crack or imperfect joint more rapidly than any other particles. This important property is well illustrated by the processes of diffusion. If hydrogen be contained in a bell-jar, of which the mouth is closed by a porous disc of




Diffusion of Hydrogen.—*a* Porous disc; *b* jar containing hydrogen; *c* coloured liquid.

plaster of Paris, whilst the narrow opening dips into water, the gas escapes through the porous disc so much more rapidly than the outer air can get in through it, that a partial vacuum is produced, and the water is rapidly sucked up into the bell-jar.

It might be supposed that a mixture of oxygen and hydrogen would gradually separate, the heavy oxygen collecting itself at the bottom of the vessel, and the hydrogen at the top. Not only does no such separation of these gases by subsidence occur, but if a flask full of hydrogen be connected tightly, by means of a long narrow tube, with a second flask containing oxygen, and the tube placed in a vertical position, with the hydrogen in the upper flask, and the oxygen in the lower one; it is found that the two




*a* Flask filled with hydrogen; *b* flask filled with oxygen.

gradually but completely mingle, in opposition to the action of gravitation.

**13.** When a cold glass bottle is passed over a flame of hydrogen, it becomes coated with a dew-like film of moisture, which is formed by the combustion of the hydrogen, and at the same time the air loses some of its free oxygen. In order to prove that the combination of hydrogen and oxygen does form water, it is sufficient to heat some cupric oxide in a glass tube, and pass free hydrogen slowly over it. The black oxide is speedily changed to red metallic copper, while the oxygen carried away from it by the hydrogen forms water which can be collected.

By taking due precautions the experiment can be conducted in such a manner as to shew exactly the weight of oxygen taken from the cupric oxide, and the weight of water formed by the combination of this oxygen with hydrogen; and it will then be found that every eight grammes of oxygen taken from the copper form nine grammes of water. So that $\frac{1}{9}$ of the weight of water is due to hydrogen, and $\frac{8}{9}$ of its weight to oxygen.

**14.** Another way of arriving at the same result is to mix oxygen and hydrogen, in the proportion of one measure of oxygen and two measures of hydrogen, and to fire the mixture by means of an electric spark in a strong glass vessel. After the explosion there will be no free hydrogen and no free oxygen left, nothing but water formed; whereas, if more than twice as great a volume of hydrogen is taken as of oxygen, the excess above the two volumes is left uncombined. By no expedient can the gases be got to combine directly with one another in any other proportion than that of one volume of oxygen to two volumes of hydrogen. Now we know that one volume of oxygen is sixteen times as heavy as one volume of hydrogen, and it follows that one volume of oxygen is eight times as heavy as the two volumes of

hydrogen with which it combines to form water. The combustion of hydrogen in air is nothing else than a process of combination of hydrogen with the oxygen of the air, forming water, and every cubic centimeter of oxygen supplied by the air unites with two cubic centimeters of hydrogen.

**15.** The combination of oxygen and hydrogen is accompanied by the evolution of intense heat; and a flame of hydrogen, fed with oxygen in the proper proportion, in a suitable burner, is used for very strong heating effects. It is generally known by the name of the oxy-hydrogen burner. A piece of lime held in the flame becomes heated to so intense a white heat as to be valuable as a source of light.

One kilogramme of hydrogen gives off in combining with the requisite weight of oxygen (8 kilogrammes), enough heat to warm 34,462 kilos. of water from 0°C to 1°C, or what is usually called thirty-four thousand four hundred and sixty-two "degrees of heat" (not degrees of *temperature*).

**16.** **Water** is seldom found in nature in a state of purity. The peculiar qualities which belong to some waters are owing to the presence of foreign substances dissolved in them. Thus sea-water contains from 3.5 to 4 per cent. of its weight of salts, which are left behind when the water itself is driven off by heat. These salts consist chiefly of sodium, potassium, magnesium, and calcium, combined partly as chlorides, partly as sulphates. Spring water presents the greatest varieties of composition, according to the nature of the soil through which it has percolated, and the substances which it has taken up. Among mineral waters which are too strongly impregnated with foreign matter to be suitable for domestic use, and are confined to medical use, chalybeate waters are those which contain iron, hepatic waters contain sulphuretted hydrogen, whilst carbonic acid gas imparts to the waters which come in contact with it at high pressures the property of effervescing. Most kinds of spring water

contain lime in solution, and possess the property of "hardness" in consequence of this lime. The hardness of water is measured by "degrees," each degree being equivalent to one grain of lime per gallon of water.

17. In order to remove mechanical admixtures with which it may happen to be contaminated, water is filtered; but for the removal of dissolved solid matter the process of distillation is most convenient.

In chemical laboratories, where water is constantly used for operations in which the presence of lime, &c., would be perfectly inadmissible, spring water is usually distilled in an iron boiler, and condensed in a coil of copper tubing lined with tin. The spray which is usually carried up by the steam from the surface of the water, ought to be allowed to collect in an intermediate chamber before the pure steam passes on to the condenser.

At sea it is now becoming more and more customary to distil sea water for the use of the crew or passengers; but when first collected from the condenser, the water, however free from saline impurities, has a peculiar sickly flavour which renders it unfit for drink. This flavour is completely removed by the customary practice of passing the water through a filter containing animal charcoal, and the water becomes charged at the same time with air, or "aerated."

For domestic use water should be kept in wooden or iron cisterns. Zinc is also used sometimes with advantage, but the use of leaden cisterns is exceedingly dangerous, especially for keeping rain water, and ought under no circumstances to be permitted.

18. It was stated above that water is the sole product of the combination of oxygen and hydrogen, and by its decomposition the oxygen and hydrogen can be recovered again, in their original quantity and with unaltered properties. The easiest way to decompose water, for the

preparation of free oxygen and hydrogen, is by the action of a strong galvanic current, on a mixture of water with sulphuric acid.

The wires which conduct the current should consist of platinum, and oxygen gas collects on the surface of one of them, rapidly rising in bubbles through the liquid, while hydrogen rises from the surface of the other. A small loss of oxygen usually occurs, but the gases are very nearly in the proportion of one volume of oxygen to two volumes of hydrogen if collected carefully.

When steam is passed through a tube intensely heated in a furnace, some of it is decomposed; but in order to collect any quantity of free oxygen and hydrogen, it is necessary to separate them from contact with one another, as soon as they are set free, as they would otherwise recombine.

For this purpose the tube through which the steam passes is made of a porous material (unglazed earthenware) and surrounded by a larger tube.

**19.** Water combines with a great variety of substances, and the term **Hydrate** is used to designate a compound of water. Thus quick lime (calcic oxide) if merely moistened with water exhibits appearances which may be compared to combustion. Intense heat is evolved, and the light powder which is formed by the combination of the lime with the water, is called calcic hydrate, or in common language, "slaked lime." The water in this compound has properties different from those of uncombined water. It is solid, and not only does it not evaporate at the ordinary atmospheric temperature, and boil at 100°C, but it requires nearly a red heat for its expulsion from the compound. When phosphoric acid is moistened with water a similar combination takes place between the two bodies forming a hydrate.

In some compounds water is supposed to be contained in a state of combination different from that in which it is held

by a strong base like lime or by an acid. For instance, the crystals obtained by evaporating a solution of metallic zinc in dilute sulphuric acid, contain water which can be driven off by heat, leaving the zinc sulphate anhydrous. This water is called water of crystallization, as it is supposed not to be chemically combined with the other materials as in hydrates.

**20.** The effects of heat upon water are very remarkable, and deserve a careful study. If water be cooled to the temperature of 0°C, which is easily done by stirring it up with pieces of ice, and then allowed to absorb heat gradually in a warm room, it will be found that the water diminishes in volume while rising in temperature, and this goes on till the water has attained the temperature of 4°C. This is the temperature at which water is heaviest; for if heated above 4°C it expands with every degree of rise of temperature. Thus a litre of water at 0°C becomes 0.99988 of a litre at 4°C, and at 9°C it has a volume somewhat greater than its original one, viz. 1.00005. Every degree further rise of temperature causes a greater proportional increase of volume; at 16°C the volume of the water is 1.00085; at 30°C it is 1.00406, at 50°C, 1.01177; at 70°C, 1.02225; at 100°C, 1.04299.

A litre measured off at 4°C expands to 1.043115 at 100°C. At 4°C the litre of water weighs 1000 grammes, called one kilogramme. At 16.$\frac{2}{3}$°C (62°F) a gallon of water weighs 70,000 grains, but at 4°C the gallon of water weighs 70007.2 grains.

When cooled to the temperature of 0°C, water can be made to give up heat, by contact with substances of a still lower temperature, but it does not for a time become colder by the process. It merely passes into the solid state, or, as we generally say, it freezes. The ice formed is however considerably bulkier than an equal weight of water: 94 grammes weight of pure ice occupy the same volume as 100 grammes

of water at 4°C, and it is customary from this circumstance to describe the density of ice as equal to 0.94.

Under favourable conditions the particles of ice arrange themselves at the moment of their formation in the form of regular six-sided prisms.

## APPENDIX TO CHAPTER II.

### PROBLEMS.

11. What is the volume of 12 grammes of hydrogen at 15°C?

12. One hundred cubic metres of hydrogen are supplied at 12°C. Wanted, the weight of a silk balloon which, when filled with the hydrogen, would press upwards with a weight of 20 grammes.

13. At what temperature has air the density which hydrogen possesses at the normal temperature (0°C)?

14. What loss of weight will 200 grammes of cupric oxide undergo by heating in contact with two grammes of hydrogen? What weight of water will be formed?

15. Four litres of hydrogen at 0°C and 760 mm. are passed over an excess of red hot cupric oxide. What loss of weight does the oxide undergo? What volume of oxygen will be wanted to supply the place of that which was carried away by the hydrogen?

16. What volume of air is required for the oxidation of that quantity of metallic copper which is reduced from its oxide by 10 grammes of hydrogen?

17. One hundred cubic centimeters of air are mixed with 50 cubic centimeters of hydrogen, and exploded by the electric spark. What is the volume of the residual mixture after explosion, supposing all the steam to be condensed?

18. What weight of potassic chlorate is required for the

evolution of that quantity of oxygen which is needed for the combustion of 10 litres of hydrogen?

19. 20 kilogrammes of water have to be heated from 0° to 1°C by the combustion of hydrogen. What weight of hydrogen is needed for the purpose?

20. 200 litres of oxy-hydrogen gas (a mixture of oxygen and hydrogen in combining proportions) are burned. What weight of water can be heated from 0°C to 1°C by the heat thus evolved?

21. An iceberg floating freely in sea-water of density 1.027 is found to have a volume of 30,000 cubic metres above water. What is the total bulk of the iceberg?

22. A block of Wenham-lake ice weighs 280 kilogrammes. What is its volume?

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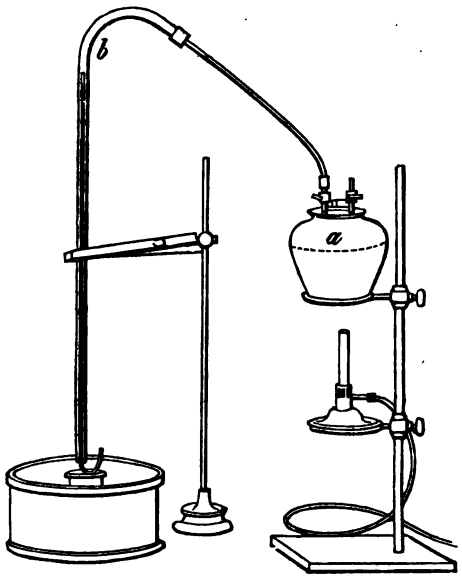
# CHAPTER III.

**21.** When water at 100°C is put over a fire, or otherwise exposed to heating action, it passes into steam, without getting hotter; so that a thermometer immersed in the boiling water continues to indicate the temperature of 100°C as long as the steam is being freely formed.

Any circumstances, however, which prevent the escape of steam enable water to undergo a rise of temperature when exposed to the action of heat. For instance, if the water be heated in a strong iron boiler, of which the outlet cock is closed so that no steam can escape, the temperature rises above 100°C; and if the boiler be strong enough to resist the force with which the steam then presses against the sides of the boiler, the water may be heated up to 200°C or 300°C, and even to still higher temperatures. If the experiment were performed in a boiler heated by a furnace and provided with a safety-valve, and if

the valve were loaded more and more heavily, so as to subject the steam to the necessity of overcoming greater and greater pressure in order to make its way out, it would be found that when heated to 120°C, the water would give off steam almost capable of lifting a valve loaded 1.033 kilogrammes on the square centimeter ($14\frac{2}{3}$ pounds on the square inch), and at a very slight elevation of temperature the valve would be lifted, and the water would boil at 120°C. By loading the valve further this ebullition could be stopped, and a load of about 3.1 kilos. on the square centimeter (44 pounds on the square inch) would prevent the water from boiling till heated to about 144°C. In like manner it would be found, that at 170°C the tension of the vapour of water is about equal to a pressure of 7.23 kilos. on the square centimeter ($102\frac{2}{3}$ lbs. on the square inch). Now if the escape-pipe from the boiler be made to communicate with a closed condenser, from which all the air has been pumped out, so that steam on making its way from the boiler, does not blow into the air, but into an empty space; it will be found that at the temperature of 100° the water in the boiler just boils when the valve is loaded 1.033 kilo. on the square centimeter ($14\frac{2}{3}$ lbs. on the square inch); and at 120°C it boils at a pressure of 2.066 kilos. ($29\frac{1}{3}$ lbs.); at 144°C it boils at 4.13 kilos. ($58\frac{2}{3}$ lbs.); and at 170°C it boils under a pressure of 8.26 kilos. ($117\frac{1}{3}$ lbs.) The removal of the atmospheric pressure by means of the air-pump, is just made up for by an additional load on the valve of 1.033 kilos. on the square centimeter, or $14\frac{2}{3}$ lbs. on the square inch, or 2126.4 lbs. on the square foot, and we are thus led to infer that the boiling-point of water is the temperature at which the tension of its vapour is able to overcome the atmospheric pressure of about 15 lbs. on the square inch. A very simple experiment confirms the truth of this conclusion. Introduce a few drops of water into the vacuum of a barometer, as shewn in the annexed figure, and gradually heat the instrument to 100°C by




Heated Barometer-tube containing water.—*a*. Boiler supplying steam; *b*. Tube conducting steam round barometer-tube.

steam. The mercury in the tube will gradually descend, and will stand at the same level inside the tube as outside it, when the water is heated to 100°C.

The tension of the vapour of water at temperatures below 100°C is measured by the depression of the column of mercury, produced by water heated to measured temperatures in the vacuum above it.

In the following table the results of observations of the tension of steam, made at low temperatures by the aid of a barometer-tube, and made at high temperatures in a strong boiler provided with a so-called pressure-gauge, are arranged in order.

The numbers given in the columns headed 'Tension in Millimeters' shew the height in millimeters of a column of mercury which could be supported by the steam.

By dividing any one of these numbers by 760 the amount of tension in atmospheres is obtained.

*Tension (or Maximum Pressure) of Water-vapour between −32°C and +230°C (Regnault).*

| Temperature. | Tension in Millimeters. | Temperature. | Tension in Millimeters. | Temperature. | Tension in Millimeters. |
|---|---|---|---|---|---|
| ° | | ° | | ° | |
| −32 | 0.320 | 55 | 117.478 | 145 | 3125.55 |
| 30 | 0.386 | 60 | 148.791 | 150 | 3581.23 |
| 25 | 0.605 | 65 | 186.945 | 155 | 4088.56 |
| 20 | 0.927 | 70 | 233.093 | 160 | 4651.62 |
| 15 | 0.400 | 75 | 288.517 | 165 | 5274.54 |
| 10 | 2.093 | 80 | 354.643 | 170 | 5961.66 |
| 5 | 3.113 | 85 | 433.041 | 175 | 6717.43 |
| 0 | 4.600 | 90 | 525.450 | 180 | 7546.39 |
| +5 | 6.534 | 95 | 633.778 | 185 | 8453.23 |
| 10 | 9.165 | 100 | 760.000 | 190 | 9442.70 |
| 15 | 12.699 | 105 | 906.410 | 195 | 10519.63 |
| 20 | 17.391 | 110 | 1075.370 | 200 | 11688.96 |
| 25 | 23.550 | 115 | 1269.410 | 205 | 12955.66 |
| 30 | 31.548 | 120 | 1491.280 | 210 | 14324.80 |
| 35 | 41.827 | 125 | 1743.880 | 215 | 15801.33 |
| 40 | 54.906 | 130 | 2030.280 | 220 | 17390.36 |
| 45 | 71.391 | 135 | 2353.730 | 225 | 19097.04 |
| 50 | 91.982 | 140 | 2717.630 | 230 | 20926.40 |

**22.** When steam is heated by itself, without the presence of any liquid water, it is called superheated steam. But when there is water present so that no excess of heat can accumulate in the steam, above the quantity needed for its formation, under the pressure at which it exists, the steam is called saturated, meaning saturated with water. And when steam is mixed with small drops of liquid water (visible as fog) it is called wet steam. When saturated steam is heated for a few degrees above the temperature at which it was formed, it expands more than oxygen or hydrogen for each degree of temperature; but at still higher temperatures this anomaly does not exist, and steam then has the coefficient of expansion $\frac{1}{273}$. It follows from this that dry saturated steam at 100°C heated to higher temperatures in a closed vessel of sufficient

strength would increase a little more than oxygen or hydrogen in pressure for each degree rise of temperature near the point of saturation.

**23.** When, however, steam and water together are heated in a closed vessel, every degree rise of temperature causes the evaporation of some additional water into the limited space occupied by the steam, and consequently an increase of the density of the steam. In order to calculate approximatively the density of saturated steam at any given temperature, it is necessary to ascertain by reference to the table what maximum pressure corresponds to the given temperature; and starting from the known density of steam at the normal temperature and pressure, to reckon its density at the given pressure by assuming it to behave like oxygen, i.e. to increase in density proportionally to the increase of pressure; then using the ordinary co-efficient of expansion ($\frac{1}{273}$) to compute how much the density calculated above would be reduced by heating the vapour from the normal temperature to that at which it has to be calculated.

**24.** The normal density of steam is best recollected in relation to that of hydrogen; for when two volumes of hydrogen weighing two grammes are combined with one volume of oxygen weighing sixteen grammes, the eighteen grammes of steam occupy just two volumes, so that each volume of steam weighs nine grammes, and steam is therefore exactly nine times as heavy as hydrogen. If it were required to calculate the density of saturated steam at 150°, we should find by reference to the table that the tension corresponding to 150°C is about $4\frac{2}{3}$ atmospheres, or 4.71 kilogrammes on the square centimeter ($4\frac{2}{3}$ times $14\frac{2}{3}$lbs. on the square inch). The increase from the normal atmospheric pressure of 1.033 to 4.71 kilos. will increase the density in like proportion, raising it from 9 to about 42. But the rise of temperature from 0° to 150°C will diminish this density in the proportion of

154.97 to 100, i.e. from 42 to 27.1. So that 27.1 is the approximative density of saturated steam at 150°, according to calculation.

25. When water evaporates into air, it is generally stated that it evaporates as into a vacuum; but this statement requires explanation. Suppose that a litre-flask were taken full of air at the pressure of 760 millimeters, and at the temperature of 15°C, and that water were allowed to evaporate into this air until it was saturated with moisture at the same temperature. It is quite true that the litre-flask would then contain the same weight of steam as if no air were there. This weight can be ascertained by a calculation perfectly similar to that shewn for the weight of one volume of steam at 150°C, and it will be found that at 15°C, and the corresponding pressure of 12.7 millimeters, the density of steam is 1.58; so that 11.2 litres weigh 1.58 grammes, and one litre of it weighs 0.141 grammes. The air in the flask continues to exert its original pressure, equal to 760 millimeters of mercury, on the flask sides, and the pressure of the steam is added to that, making the whole pressure $760+12.7=772.7$ millimeters.

When, on the other hand, bubbles of air pass through water in an open vessel, the moist bubbles which are formed expand immediately to a greater volume than the dry air from which they were formed, by the addition of steam. The moist air is therefore at the same pressure as the original dry air, but has gained in volume as much as, if enclosed in a flask, it would have gained in pressure by taking up steam. Thus, if a litre of air at 15°C and 760 millimeters mercurial pressure bubbled through water at 15° in an open vessel, the moist bubbles formed would occupy a volume greater than the litre in the proportion of 760 and 772.7, viz. 1.0167 litres, while remaining at the same temperature.

The pressure of air is measured by the barometric pressure

to which it is subjected. This we may call B, and the tension of the steam corresponding to the temperature of the experiment may be called T. Then the air in the moist bubbles has a pressure B—T, while the tension of the steam makes up the loss of pressure caused by the expansion of the air.

The boiling-point of water was described above as the temperature at which the tension of steam is equal to the atmospheric pressure, so that the slightest addition of heat to any part of the water causes it to form bubbles of steam, and to lift the atmosphere enough to make room for those bubbles. But when water evaporates into oxygen or hydrogen gas at constant pressure, and forms a mixture of greater volume than the original dry gas, there is truly a lifting of the atmosphere to make room for the steam thus formed, as much as if it were by itself and unmixed with the permanent gas. So that at temperatures below its boiling-point water does evaporate and lift the atmosphere if in sufficiently close contact with a permanent gas, but only to such an extent that its volume, calculated at atmospheric pressure, stands to the volume of the permanent gas in the same proportion as the tension of the steam stands to the barometric pressure.

**26.** When aerated water is gradually heated in a glass vessel it gives off small bubbles of air before actually beginning to boil; and it must be kept briskly boiling for several hours, and cooled in a vessel to which atmospheric air has no access, if wanted perfectly free from air. If then brought in contact with oxygen gas at 0°C, it would dissolve about 4 per cent. of its volume of that gas. At 10°C it dissolves only $3\frac{1}{4}$ per cent. of oxygen, and at 20°C about 2.8 per cent. This dissolved oxygen is driven out again, with its original properties, by prolonged boiling.

Hydrogen is rather less than half as soluble as oxygen at

0°C; for 100 volumes of water take up, according to Bunsen, 1.93 volumes of hydrogen, but at 10° and 20° the same volume is dissolved. Whether the experiment is tried at the atmospheric pressure or at a higher pressure, water still dissolves these same volumes of the gases and weights proportional to the pressure. Hence it is that water saturated with oxygen under pressure effervesces as soon as the pressure is removed, and only retains in solution the quantity of gas corresponding to the lower pressure.

## APPENDIX TO CHAPTER III.

### PROBLEMS.

23. Ascertain from the tables the tension of steam at the following temperatures, viz. 70°C, 120°C, 140°C, 180°C; and calculate the density corresponding to each of these temperatures.

24. What is the density of steam at 760 mm. pressure, superheated to 200°C?

25. A room contains 80 cubic meters of air, saturated with moisture at 12°C and 760 mm. pressure. What would be the volume of the air by itself, at the same temperature and pressure, after removal of the moisture?

26. A glass globe of 10 litres capacity is full of dry air at 100°C and 760 mm. pressure. Water is forced into it as long as it evaporates, the temperature being kept at 100°. What will be the tension of the moist air?

27. A mixture of air and steam is wanted containing one volume steam to two volumes air; and in order to obtain such a mixture it is proposed to bubble air through water kept uniformly at a temperature such that its vapour has the tension necessary. What is the temperature to which the water must be heated?

28. A subterranean cavity contains 30 cubic metres of

water, at the temperature of 10°C. Hydrogen gas is bubbling through this water, and escaping afterwards at a pressure equal to 7,600 mm. of mercury. What weight of hydrogen will be dissolved in the water when it is fully saturated?

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# CHAPTER IV.

**27.** The quantity of heat which water requires in order to undergo a rise of temperature of one degree centigrade is used as a measure of the quantity of heat which other substances require for 1°C elevation of temperature, and the term "one degree of heat" means that quantity which heats one kilogramme of water from 0°C to 1°C. A kilogramme of oxygen undergoes 1° rise of temperature by about $\frac{1}{5}$ of a degree of heat; that is, it needs only about enough heat to warm $\frac{1}{5}$ of a kilogramme of water from 0°C to 1°C. The number 0.2182 represents the exact quantity as determined by Regnault, and is usually referred to as the specific heat of oxygen. Hydrogen has the highest specific heat of all known substances, the co-efficient being 3.4046. It is convenient to represent the specific heat of these two gases by volume instead of by weight; and as 16 parts by weight of oxygen occupy the same volume as 1 part by weight of hydrogen, we have only to multiply by 16 the specific heat of oxygen, in order to get the quantity of heat absorbed by 16 kilos. of oxygen, which are equal in volume to 1 kilo. of hydrogen. Now $16 \times 0.2182 = 3{,}4912$, which is nearly the same as the heat absorbed by an equal measure of hydrogen. The specific heat of steam is 0.4805, or rather less than half that of water. It is worthy of note that the oxygen and hydrogen contained in 9 kilos. of steam have, before combination, specific heats amounting together to 5.149, whereas

the specific heat of 9 kilos. of the combined gases is only 4.3245.

Ice has a specific heat of 0.504 if examined between 0°C and −20°C, but if examined for the whole range of temperature from 0°C to −70°C it has a mean specific heat of smaller amount, viz. 0.474.

A careful comparison of the specific heat of water at different temperatures has shewn that at high temperatures the specific heat is somewhat greater than at low temperatures, as will be seen by the following examples calculated from a general formula which agrees with the observations—

at 0°C sp. H=1.0000; at 50°C sp. H=1.0042.
at 100°C sp. H=1.0130; at 150°C sp. H=1.0262.
at 200°C sp. H=1.0440; at 230°C sp. H=1.0568.

Oxygen has the same specific heat at high temperatures as at low temperatures, and the same assertion no doubt holds good with regard to hydrogen. Oxygen is also found to have the same specific heat when examined under great pressure as when examined at its ordinary pressure and density.

**28.** The apparatus used for determining the specific heat of gases is so arranged as to allow the gas under examination to expand while it is being heated, and to contract again while it is giving up its heat to the calorimeter for measurement. In this manner the gas is kept at a constant pressure (measured by the barometer at the time of experiment). If a kilogramme of oxygen were enclosed in a strong bottle, and heated without being allowed to expand, it would be found to have a smaller specific heat, viz. about $\frac{5}{7} \times .2175$, or .15; and in like manner a kilogramme of hydrogen if heated without expansion would have a specific heat, $\frac{5}{7} \times 3.409$. In other words, oxygen or hydrogen require about $\frac{2}{7}$ more heat if allowed to expand while they are being heated 1°C, than if heated without expansion. Representing as 1 the specific heat of these gases at constant volume, the specific heat at

constant pressure is represented by the fraction 1.413. An example will help us to understand this wonderful law.

**29.** Let a kilogramme of oxygen be heated from 0°C to 100°, and while expanding, let it drive before it a column of mercury 760 millimeters long, in a vertical tube of one square centimeter area. This column of mercury weighs 1.033 kilogrammes; to that a weight of 1.033 kilos. is raised one meter, by every 100 cubic centimeters increase of volume of the gas. Now as 16 grammes of oxygen measure 11.2 litres at 0°, the thousand grammes which are to be expanded measure $\frac{11.2 \times 1000}{16} = 700$ litres at 0°C, and their increase of volume in expanding to 100° is $\frac{36.65 \times 700}{100} = 256.55$ litres or 256550 cubic centimeters. As the expansion takes place in a tube of one square centimeter area, the oxygen raises a weight of 1.033 kilos. to a height of 2565.5 meters, and does $1.033 \times 2565.5 = 2650.16$ meter kilogrammes of work; or in other words, the kilogramme of oxygen in expanding from 0° to 100° does work equivalent to that of raising one kilogramme to a height of 2650.16 meters.

**30.** The mechanical force expended in raising this weight can be recovered again, if the weight be allowed to fall, for the falling mercury might be made to turn a wheel, or some other suitable mechanism, so as to set other masses in motion, by the momentum which it accumulates in falling. It has been proved by Mr. Joule that if mechanical force be employed in agitating water, so that the particles of the water rub against each other and get heated by friction, every 423.6 meter kilogrammes of work so expended produces one degree of heat; that is to say, enough heat to raise the temperature of one kilogramme of water from 0° to 1°C. 423.6 meter kilogrammes accordingly represent the "mechanical equivalent" of one degree of heat. Whenever heat

is transformed into mechanical force, by the expansion of a gas which lifts the atmosphere while expanding, or by any other process, every degree of heat so expended produces 423.6 meter kilogrammes of work.

The knowledge of the mechanical equivalent of heat, enables us to calculate how much heat is consumed by the work which the kilogramme of oxygen does in expanding. That work was computed at 2650.16 meter kilogrammes, and every 423.6 of these is equivalent to one degree of heat, so that $\frac{2650.16}{423.6} = 6.25$ is the quantity of heat which is transformed into mechanical work, when one kilogramme of oxygen expands and raises the atmosphere by being heated from 0° to 100°C. The heat absorbed by the kilogramme of oxygen is partly employed in heating it, partly in doing the work of lifting the weight of the atmosphere. This total quantity of heat is found by multiplying the specific heat of oxygen at constant pressure (0.2175) by the number of degrees that it is heated (100), and accordingly 21.75° is the total quantity of heat absorbed by the oxygen.

It was stated above that the specific heat of oxygen at constant volume is to its specific heat at constant pressure in the proportion of 1 to 1.41, and accordingly if the kilogramme of oxygen had been heated from 0° to 100° in a closed vessel, so that it could not do any work, it would only have absorbed $\frac{21.75}{1.41} = 15.4°$. The difference between this quantity of heat and 21.75 is 6.35°, or very nearly that same quantity of heat which from the work done by the expansion of the oxygen, and the mechanical equivalent of heat, was computed to have been needed for the effort of expanding the oxygen, so as to keep it at atmospheric pressure while heated from 0° to 100°.

31. There are other and more direct means of proving

that oxygen by expanding under pressure is an agent for the transformation of heat into mechanical work; for if a delicate metallic thermometer of Breguet's construction be introduced into a bell-jar containing oxygen over mercury, and if the bell-jar be suddenly raised by the hand so as to expand the gas without letting it out of the bell-jar, the thermometer will shew a fall of temperature. In this experiment the hand of the operator only applies enough force to lighten the pressure of the bell-jar, and of the air on the oxygen, sufficiently to enable the expanding oxygen to lift them; and the expanding oxygen does aid in producing the mechanical effect of raising these weights, and does use up heat in doing this work.

Heat which thus disappears for the production of mechanical work may be called latent whenever it can be recovered again by reversing the process. Whenever oxygen or hydrogen are compressed, there is an expenditure of mechanical work incurred, and the exact equivalent of this expended work makes its appearance as heat in the compressed gas.

If the experiment of expanding the kilogramme of oxygen were to be carried on so as to bring matters back to their original state, it would only be necessary to abstract heat from the heated oxygen, by putting it in contact with some cold surface, say metallic tubes kept at 0°C by ice-cold water circulating through them. The weight of 1.033 kilogrammes would begin to fall from its full height (2565.5 meters) as soon as the oxygen began cooling, and it would have fallen through 2565.5 meters as soon as the kilogramme of oxygen was cooled down to 0°C. The heat taken out of the oxygen by this time would be 21.75°C, that is, not only what it had retained while heating to 100°C, but also the 6.25° which it had been an agent for transforming into work. The 1.033 kilos. of mercury in falling compress the oxygen and evolve the 6.25° of heat by expenditure of mechanical work. Similar

principles apply to the expansion of steam by rise of temperature, and its condensation by cooling agents. In order to make the comparison we will take the same volume of steam at 100° which we just now took of oxygen at 0°, viz. 700 litres, and heat it until it expands to a volume greater by 256.55 litres, so that the steam will do the same amount of work in expanding which was done by the oxygen. We will assume that the steam expands at the same rate for each degree rise of temperature, which is only an approximation to the truth.

In order to gain 256... litres in volume by rise of temperature from 100° the steam must be heated to 236.3°.

The weight of 700 litres of steam at 100° is calculated at 415.3 grammes*; and taking the specific heat at 0.4805 for the rise of temperature from 100 to 236.3, it appears that the steam absorbs rather more than 27°. When 6.3° is deducted from this quantity as equivalent to the work done in expansion, there remains 20.7° as absorbed by the steam, which is more than the quantity absorbed by the oxygen, on doing an equal amount of work.

Another difference between steam, and either oxygen or hydrogen, would be discovered by allowing saturated steam to expand, by a gentle diminution of the pressure upon it. The steam would give up heat, and transform it into mechanical force, but in doing so, some of the steam would be condensed into water, as would be seen by a foggy appearance after expansion. Superheated steam presents no condensation of water on expansion, but becomes cooler by doing work just like oxygen, till its temperature is lowered to the point of saturation.

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* According to the observations of the density of steam, Rankine assigns to a cubic foot at 100° the weight 0.03797 of a pound, which corresponds to 421.3 grms. as the weight of 693.75 litres.

If pressure be applied to saturated steam it becomes hotter, but the heat evolved by the expenditure of mechanical force can be removed from the steam, and its temperature maintained constant, while its volume is being reduced by pressure. In this case the density of the steam will remain perfectly constant, and the diminution of its volume will be effected by the condensation of steam into water.

The term 'vapour' is usually applied to those aeriform bodies which are made by the action of heat upon liquids, and which return to the same liquid state, either by removal of heat or by pressure.

**32.** It was stated above that water does not become hotter by continuing to boil, and moreover the steam which escapes is no hotter than the water itself, so that the heat which passes into it produces the change of water at 100°C into steam at 100°C while disappearing thermometrically. When saturated steam at 100°C is compressed as above described, so as gradually to be condensed into water, and the mixture kept at 100°C until all the steam has been liquified, all the heat is recovered which had disappeared during the evaporation of the water; so that the heat is called "latent," to convey the idea that it is stored up in connection with the steam, so as to be recoverable when the steam returns to the state of water.

A very simple experiment serves to measure approximately the latent heat of steam. Put $5\frac{1}{3}$ kilos. of ice-cold water into a jar, and blow steam into it till no more can be condensed. Then weigh the boiling-hot water thus obtained. The first portions of steam condense to water, and are cooled by mixing with the ice-cold water, but at the end of the experiment the original $5\frac{1}{3}$ kilos. of water, together with the water formed by condensation of the steam, are left at the temperature of 100°C; so that the steam may be considered to have been condensed without becoming cooler, and to have evolved $5\frac{1}{3} \times 100°C = 533°$ of heat by its condensation.

The increase of weight is nearly one kilo.; so that one kilo. of steam condenses to water of the same temperature, evolving about 533 degrees of heat.

**33.** At temperatures above 100°C and all corresponding pressures, more heat is required to transform water at 0°C into steam. The quantity of heat for different temperatures is given by Regnault's formula, $606.5° \times .305\ t°$; which means that the number of degrees centigrade at which the saturated steam is to be formed is to be multiplied by .305 and added to the number 606.5, in order to shew how many degrees of heat are required for heating one kilogramme of water from 0° up to the given boiling-point and evaporating it at the pressure corresponding to that boiling-point. Thus to heat water at 0°C up to 100°C and evaporate it, we have $606.5° + 30.5° = 636.5°$; to heat it up to 200°, and evaporate it at that temperature, 667.5°C are required; and at 0°C every kilo. of water absorbs only 606.5° of heat in evaporating.

**34.** In the process of freezing water, heat is also given off, and the same quantity of heat is absorbed again when it is melted. A kilo. of water on cooling from 80°C to 0° gives off enough heat to melt one kilo. of ice at 0°C, the two kilos. of water which are thus obtained being at the same temperature (0°) as the ice before fusion. The heat which water gives off on becoming ice can be made to boil liquids: for instance, ether can be made to boil at temperatures below 0°C if put in contact with a vessel containing water, while the pressure of the atmosphere is removed from the surface of the ether by a good air-pump. Ice-making machines have been constructed on this principle; the ether vapour which is pumped out of the boiling ether being subsequently compressed into a condenser tube, and thus recovered for repeated use.

Water can also be frozen by the evaporation of some of its particles. For this purpose an instrument called a cryophorus is constructed. It consists of two glass bulbs

connected by a glass tube and hermetically sealed. One of the bulbs is about half full of water, and the remainder of the space in the apparatus contains nothing but steam, all the air having been expelled by long boiling, before the apparatus was closed. The bulb containing steam can be brought to a temperature considerably below 0°C by immersion in a so-called frigorific mixture, and the steam in it is thereby condensed. Fresh steam then comes over into the cold bulb from the one containing water, and steam is formed by evaporation of some of the water under the greatly reduced pressure, till the remaining water has at last parted with all its latent heat of fluidity and has become ice.

## APPENDIX TO CHAPTER IV.

### PROBLEMS.

29. How many "degrees of heat" are required to raise the temperature of 4 cubic meters of oxygen from 0°C to 100°C? What increase of volume will the oxygen undergo?

30. What weight of hydrogen would you have to burn in order to evolve enough heat to heat 100 kilogrammes of steam from 120°C to 200°C?

31. What quantity of heat is obtained by cooling 90 grammes of hydrogen from 300°C to 0°C?

32. A kilogramme of hydrogen is heated from 0°C to 100°C, at the atmospheric pressure of 1.033 kilo: on the square centimeter. How much work (in meter kilogrammes) does it do in expanding?

33. How many degrees of heat are evolved by the fall of a thousand kilogrammes from a height of ten meters?

34. Translate into its equivalent of mechanical force the heat evolved by the combustion of 500 grammes of hydrogen.

35. Calculate the quantity of heat required to heat a kilogramme of water from 0°C to each of the following temperatures

and to evaporate it at each temperature (under corresponding pressure):—viz. 150°C, 250°C, 50°C.

36. A pond is calculated to contain 1100 cubic meters of ice. What quantity of heat will be required to melt it?

37. What weight of saturated steam at 100°C is needed for the fusion of a kilogramme of ice?

38. Ten kilogrammes of oxygen at 100°C have to be cooled to 0°C. What weight of ice will be required for the purpose?

39. What quantity of heat will be needed to raise the temperature of a kilogramme of oxygen from 0°C to 100°C in a closed and inextensible vessel?

40. How much mechanical force will be required to condense water by pressure 100 cubic meters of steam saturated at 100°C? The heat evolved by compression is removed as fast as it is evolved.

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# CHAPTER V.

**35.** The letter O is used to denote an atom of oxygen, and in like manner H denotes an atom of hydrogen. An explanation of the term 'atom' will be given when a sufficient number of substances have been described to afford materials for the explanation. Meanwhile it is sufficient to define O as sixteen parts by weight, for instance, 16 grammes of oxygen; and H as one part by weight, say 1 gramme of hydrogen. The symbol attached to the name of each element in the list at p. 100, means in like manner an atom of that element. The weight of each atom is appended to its symbol. The juxtaposition of two symbols is used to denote combination of the respective atoms: thus, $H^2O$ means a compound of

two atoms of hydrogen, each weighing one, with one atom of oxygen weighing sixteen.

**36.** The quantity of water represented by this formula is called a molecule; and the molecule of a compound or of an element is the smallest quantity which can exist by itself, or take part in any process.

Every molecular formula, like $H^2O$, denotes a weight of the compound equal to the sum of the weights of the atoms contained in it, so that $H^2O$ means 18 parts by weight of water. The molecule of water occupies, however, in the state of vapour exactly two volumes, whereas the three atoms which go to make it occupy together three volumes while uncombined. The vapour volume of all molecules is the same as that of the molecule of oxygen or of hydrogen, and is called two volumes, so that it is not found by adding together the volumes of the atoms combined in the molecule.

**37.** The sign + interposed between symbols denotes addition or mixture of the atoms or molecules which the symbols represent, and in the proportions by weight corresponding to those symbols. In like manner the sign — between two symbols denotes the removal from one another of the atoms or molecules in the proportions described. The sign = is used in describing chemical changes. It only denotes equality in weight, between the sum of the atoms of each kind on one side of it and the sum of the atoms of the same kind on the other side of it. Thus $H+O$ denotes a mixture of 1 part by weight of hydrogen with 16 parts by weight of oxygen. $H^2+O=H^2O$ means that 2 parts by weight of hydrogen, added to 16 parts by weight of oxygen, can be made to combine to form 18 parts by weight of water. $H^2O-O=H^2$ means that if 16 parts by weight of oxygen are taken away from 18 parts by weight of water, 2 parts by weight of hydrogen are formed.

Brackets are frequently used to facilitate the comparison of two formulæ. Thus in comparing the formulæ $(SO^4)$ Zn and $(SO^4)H^2$, the use of brackets inclosing those constituents which are common to the two salts, serves to mark the fact that the difference between them is that one has got $H^2$, two atoms of hydrogen, while the other has got Zn, one atom of zinc. When several symbols are enclosed by brackets, and a number put after the group, the whole group is multiplied by that number.

**38. Hydric Peroxide** ($H^2O^2$). Oxygen and hydrogen do not unite directly in any other proportion than that in which they form water, but by indirect means a molecule of water can be made to combine with an atom of oxygen, forming hydric peroxide. For the preparation of this remarkable compound, baryta peroxide ($BaO^2$) should be ground to a fine powder under water, and left for some time in contact with the water. A combination takes place forming a hydrated peroxide ($BaH^2O^3$). When this hydrate is dissolved in dilute hydrochloric acid, baryta chloride is formed, together with hydric peroxide—

$$BaH^2O^3 + (HCl)^2 = Cl^2Ba + H^2O^2 + H^2O.$$

The baryta chloride can be removed from the solution by carefully dropping into it a solution of argentic sulphate as long as it continues to form a precipitate. The two soluble salts exchange metals, forming baryta sulphate and argentic chloride, both of which are insoluble—

$$BaCl^2 + Ag^2SO^4 = (AgCl)^2 + BaSO^4;$$

and they settle at the bottom of the liquid, if it be allowed to stand; so that the solution of hydric peroxide can be poured off clear. In order to get rid of the greater part of the water which is mixed with the peroxide, the liquid is put into an open porcelain dish, under a glass bell-jar fitted onto the plate of an air-pump. A vessel containing strong oil of vitriol is also put under the bell-jar, and the air is then

pumped out from it. In this vacuum the water evaporates rapidly, and is absorbed by the oil of vitriol, forming with it a compound far less volatile than water itself. In this manner a concentrated solution of peroxide is finally obtained of a specific gravity of 1.45, which bleaches litmus-paper.

**39.** This solution is rapidly decomposed by heat, giving off oxygen, and leaving water. It is also decomposed by various substances at the ordinary temperature. Thus, charcoal causes an immediate effervescence of oxygen in the solution, and finely-divided platinum, in the form called platinum black, decomposes it still more rapidly. It is worthy of remark that the charcoal or platinum is found unchanged at the end of the decomposition, and although the peroxide gives up oxygen with the utmost readiness, it does not always allow other substances to combine with the oxygen which it is giving off. It frequently induces compounds containing oxygen to undergo a decomposition similar to its own, and to give off oxygen. Thus, potassic chromate when dropped carefully into an acid solution containing hydric peroxide, is changed at first into a deep-blue body, and immediately afterwards turns green by giving off half its oxygen with the oxygen which is escaping from the peroxide. Still more remarkable is the action of the peroxide on the oxides of manganese: a mixture of peroxide of manganese with nitric acid is deoxidized by hydric peroxide. Half of the oxygen which is given off comes from the hydric peroxide, whilst the other half comes from the binoxide of manganese. The protoxide of manganese formed in this reaction is reconverted into binoxide by the action of hydric peroxide, in presence of an alkali or substance opposite to acids in its properties.

These remarkable phenomena have been investigated by Professor Brodie, and explained by him as due to the fact

that oxygen from the one body combines with oxygen from the other, forming free oxygen, of which the molecule $O^2$ contains two atoms.

## APPENDIX TO CHAPTER V.

### PROBLEMS.

41. State in words the meaning of the following equations (ascertaining the signification of each elementary symbol from the table of atomic weights):—

$$H^2O + Na = Na\,H\,O + H;$$
$$Cl^2 + H^2O = Cl\,H + Cl\,H\,O;$$
$$Ba\,Cl^2 + H\,T\,O^4 = Ba\,S\,O^4 + (H\,Cl)^2;$$
$$Na\,Cl + H\,T\,O^4 - H\,Cl = H\,Na\,S\,O^4.$$

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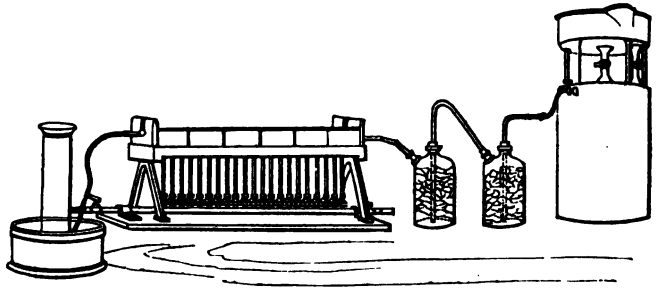
# CHAPTER VI.

**40. Nitrogen** ($N^2$, $N = 14$), in the free state, is one of the most inert of gases, and is described by its inability to burn or to support combustion, and generally by its disinclination to combine.

When combined with oxygen and hydrogen it forms a strongly acid compound called nitric acid; and with less oxygen and more hydrogen it forms the compound called ammonia hydrate, which is a strong base, or in other words a strongly anti-acid substance.

Nitrogen is the chief constituent of atmospheric air, and is best prepared from that source. A tube containing metallic

copper, as obtained by the reduction of cupric oxide by hydrogen, is heated to redness, and a current of purified atmospheric air is then passed slowly into it at one end; pure nitrogen passes out at the other end. The purification of the air is effected by first passing it through a plug of cotton-wool in a tube, so as to strain off particles of dust, &c., which are contained in it, and then through a long tube, containing solid potash, for the absorption of carbonic acid, and finally



Preparation of Nitrogen from Air.

through a third long tube containing pumice moistened with strong sulphuric acid for the absorption of water and ammonia. The oxygen is entirely absorbed by the metallic copper, and pure nitrogen can be collected as it escapes from the tube.

**41.** By arranging this experiment suitably, the relative weights of oxygen and nitrogen in air can be determined with great accuracy. For this purpose a large glass globe, fitted with a good stop-cock, is exhausted by means of an air-pump, and then weighed. It is then connected with the end of the tube containing metallic copper, in such a way that all the nitrogen which passes through the tube shall go into the globe. The tube containing copper must also be weighed before it is connected with the globe. As soon as the tube of copper is red hot, purified air is allowed to

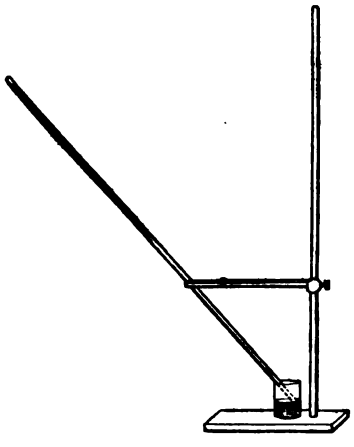
pass slowly through it. All the oxygen is deposited on the copper, while the nitrogen goes over to the exhausted globe. At the end of the experiment the globe is weighed again, and its increase of weight shews how much nitrogen there was in the air; the tube containing copper, now partially oxidised, is also weighed, and its increase of weight shews the quantity of oxygen in the air.

| | by volume | by weight | |
|---|---|---|---|
| 100 parts of air contain | 20.9 | 23.1 | of oxygen. |
| | 79.1 | 76.9 | of nitrogen. |

Nitrogen is somewhat lighter than air; its density is 14, the density of air being 14.4.

When heated at constant pressure nitrogen expands in the same proportion as oxygen and hydrogen for each degree rise of temperature, and the quantity of heat which one volume of it absorbs in order to undergo a rise of temperature of one degree is the same as the quantity absorbed by one volume of oxygen or of hydrogen. Nitrogen increases in density proportionally to the pressure to which it is subjected, and the greatest pressure and cold to which it has been subjected have failed to condense it to the liquid state.

**42.** The weight of the sea of air, or atmosphere, as it is generally called, is best investigated by means of a mercury barometer. A straight glass tube, nearly one meter long and closed at one end, is filled with mercury, care being taken to remove all the bubbles of air which at first adhere to its sides, by sweeping them away by means of one large bubble. The open end of the tube is then closed by the finger till dipped under mercury in a little cup. If the tube be then held vertically the mercury in it will fall several inches below the top of the tube; but by inclining the tube the mercury can be made to fill the whole of it. In each position of the tube the column of mercury inside it will



Moveable barometer to shew uniform height of mercurial column, with varying lengths.

be 760 millimeters (30 inches) measured vertically above the mercury in the cup, if the tube be long enough to allow it to rise to that height. When such a barometer is carried up to a height, so that there is a shorter column of air above it, the mercury falls; and in like manner the mercurial column rises to a greater height when the barometer is taken down any deep well or shaft.

When the barometer is put under a bell-jar, and a part of the air contained with it gradually pumped out, so that the portion of air remaining in the bell-jar is of lesser and lesser density and corresponding pressure, the mercury falls in proportion to this diminution of tension. Thus, if the mercury stood first at a height of 760 millimeters (30 inches) the removal of half the air from under the bell-jar would lower the pressure of the remainder to $\frac{1.033}{2}$ kilo. on the square centimeter ($\frac{14.7}{2}$ lbs. on the square inch), and the mercury would fall to 380 millimeters (15 inches). If $\frac{9}{10}$ of the air were removed from the bell-jar, the mercury would stand at a height of 76 millimeters (three inches) only, the pressure of the remaining air on the surface of the mercury in the cup being 0.1033 on the square centimeter (1.47 lbs. on the square inch).

A perfect vacuum would not support the mercury in the barometer at all, but even the best air-pumps are not perfect,

they leave enough air to support half a millimeter or sometimes less height of mercury.

**43.** According to the results of Regnault's experiments, a cubic meter of dry air, measured at 0°C and 760 millimeters, mercurial pressure, weighs 1.2932 kilogrammes (or 100 cubic inches of dry air, measured at 0°C and 29.92 inches mercurial pressure, weigh 32.586 grains). In a cubic meter of air there are 10,000 columns of air of one meter high and of one square centimeter section, each of which weighs 0.00012932 of a kilogramme. In order to make up 1.033 kilos. (the actual weight of the air on each square centimeter) we should need 8,020 such columns of air one meter long, or a column of uniform density about 8,020 meters high. If the upper strata of the atmosphere were of this density as well as the lower strata, the height of the atmosphere would be 26,315 feet, or five miles all but 85 feet, above the level of the sea. But each stratum of air has a density proportional to the superincumbent weight, and the higher strata have consequently a lesser density than the lower ones. If a bottle of one litre capacity were taken up to a mountain (about 18,000 feet) 5,486 meters high, while kept at 0°C, and there filled with air at 0°C, it would only take in half as great a weight as if filled on the level of the sea, viz. $\frac{1.2932}{2}$ grammes, because the stratum of air at that height has only half as great a pressure upon it as the lower air, and consequently only half as great a density. If the mouth of the vessel were closed by immersion in a vessel of mercury it would be found that on the level of the sea half a litre of mercury would be forced into the bottle by atmospheric pressure; so that the enclosed air would be at double as great a density as when collected on the top of the mountain. It is assumed that the level of the mercury inside the bottle is kept equal to the level outside, so as not to interfere with the atmospheric pressure on the contents of the

bottle. It is computed that the air extends to a height of about (130,000 feet) 39,624 meters, and that it is prevented by its own weight from expanding still further into the vacuum beyond it.

**44.** The temperature of the atmosphere is lower in elevated strata than near the surface of the earth, and this is easily accounted for by the fact that the air absorbs but a small part of the heat which is brought by it to the sun's rays, while the greater portion of the heat passes through the atmosphere, and heats the surface of the earth, or produces changes in its materials. The lower strata get heated in the day-time by contact with the hot ground, until their expansion renders them lighter than the upper strata, when a circulation immediately establishes itself. The evaporation of water in the lower atmospheric strata also causes a circulation, for the density of steam is less than $\frac{2}{3}$ that of air, and moist air is therefore lighter than dry air.

**45.** In the night-time, while the surface of the ground is receiving no heat from the sun, it is constantly giving off its heat, in the form of rays, more especially when the air above it is clear; and the lower strata of air are then cooled by contact with the cold earth. This cooling action often proceeds far enough to cause a condensation of moisture from the air, in the form of dew.

The formation of dew from the air is best studied with the aid of a hygrometer. Daniell's hygrometer is a kind of cryophorous containing ether, and having one bulb blackened internally while the other bulb is covered by cambric. This cambric bulb is gradually cooled by dropping ether onto it until moisture begins to be deposited from the air on the blackened bulb. A small thermometer contained in the ether of the blackened bulb is then read off, and at the same time a thermometer in the outer air is read off. The difference between the two readings shews how

much the air had to be cooled in order to begin to deposit moisture.

The temperature at which air begins to deposit moisture is called the dew-point. When the dew-point is many degrees below the temperature of the air, the air is capable of taking up more moisture, or, in other words, it is capable of drying a moist surface more rapidly than when the dew-point is but few degrees below the prevailing temperature. Thus it is that air containing a given quantity of moisture would be practically considered drier at 24°C than at 16°C.

If the dew-point of this air were at 16°C, or in other words if it contained as much steam as it could hold dissolved at 16°, it would have no drying action at that temperature, but a considerable one at 24°.

The quantity of steam dissolved in the air is too variable to admit of being estimated in any particular case by an average from many observations. In this country such an average would perhaps be about 1.5 per cent. of the volume of the air.

**46.** Two other essential constituents of air are carbonic acid and ammonia. 100 volumes of air usually contain about 0.04 of carbonic acid; but its proportion is in many localities greater, and in ill-ventilated rooms is said to vary from 0.1 to 0.4, and even 0.7.

The respiration of animals not only removes oxygen from the air but replaces it by carbonic acid. Herbivorous animals usually exhale carbonic acid, in volume equal to the oxygen which they absorb, but carnivorous animals appear to exhale a volume of carbonic acid smaller by 40 per cent. than that of the inhaled oxygen.

Dumas states that a man absorbs 220 to 245 cubic centimeters (from 13½ to 15 cubic inches) of oxygen per minute, which amounts to a little more than 450 grammes (or about one pound) per day. From 100 cubic centimeters of inhaled

air, a quantity of oxygen varying from 4 to 6 cubic centimeters are usually removed at each inspiration. The average weight of water exhaled from the lungs per day is upwards of 500 grammes (or 8,000 grains), while that of carbonic acid is somewhat greater, viz. 550 grammes (or 8,500 grains).

To keep an inhabited room in a state of good ventilation for one person, 283 litres (10 cubic feet) of air should be removed every minute, and replaced by fresh air.

The proportion of ammonia in air is far smaller and also more variable than that of carbonic acid. Ten million volumes of air have been found to contain from 1.3 to 3.3 volumes of ammonia. Both carbonic acid and ammonia are given off and oxygen absorbed by decomposing vegetable and animal matter, and in some districts carbonic acid is evolved from vegetable matter underground, when it comes in contact with water at high pressure, and gives rise to the effervescing springs. The processes of combustion of wood and coal which are now carried on for heating and mechanical purposes on a vast and increasing scale, constitute another drain of oxygen from the air and supply of carbonic acid.

**47.** The continual consumption of atmospheric oxygen in these various ways would gradually diminish its quantity, while replacing it by carbonic acid, were it not for the respiration of plants. Under the influence of sunshine, the leaves of plants absorb carbonic acid, and give off oxygen. At the same time plants feed upon ammonia, and by their vital processes the elements of these substances and of water are elaborated into the varied compounds which we extract from plants—such as sugar, starch, wood, volatile oils, fatty oils, gluten, &c., &c. The processes by which these substances are formed might be called processes of unburning; for they are exactly the opposite processes of combustion. Not only do plants produce these combustible compounds while

liberating oxygen, but they absorb from the sun's rays a vast quantity of heat, which they render latent, or store up in the form of wood and oils, &c., and of free oxygen.

The water of the sea, as well as of rivers and lakes, holds both oxygen and nitrogen in solution, and this air serves to support the respiration of fishes. It is richer in oxygen than atmospheric air, for 100 volumes of it contain upwards of 33 volumes of oxygen. This difference is owing to the fact that water dissolves nitrogen less freely than it does oxygen. At 0°C 100 volumes of water dissolve about 2 volumes of nitrogen; at 10°C only 1.6 volumes; and at 20°C, 1.4: in each case about half as much as of oxygen. Marine plants absorb the carbonic acid, which is exhaled by fishes, and give off oxygen in its stead, thus helping to keep the composition of the air in water suitable for the respiration of the fishes.

## APPENDIX TO CHAPTER VI.

### PROBLEMS.

42. 50 cubic meters of nitrogen are in a jar holder, and it is desired to add enough oxygen to make a mixture of the same composition as atmospheric air. How much potassic chlorate will be needed for the purpose?

43. An experimentalist fills with dry and pure atmospheric air at the temperature of 10°C a bottle of one litre capacity at a height in the atmosphere such that a barometer stands at a height of 350 millimeters. What volume of oxygen and what volume of nitrogen will he leave in his bottle at the normal temperature and pressure?

44. Atmospheric air at the temperature of 15°C, and of which the dew-point is at 10°C, is passed over a moist surface of earth. What weight of water can each cubic meter of this air take up, supposing its temperature to remain at 15°C?

# CHAPTER VII.

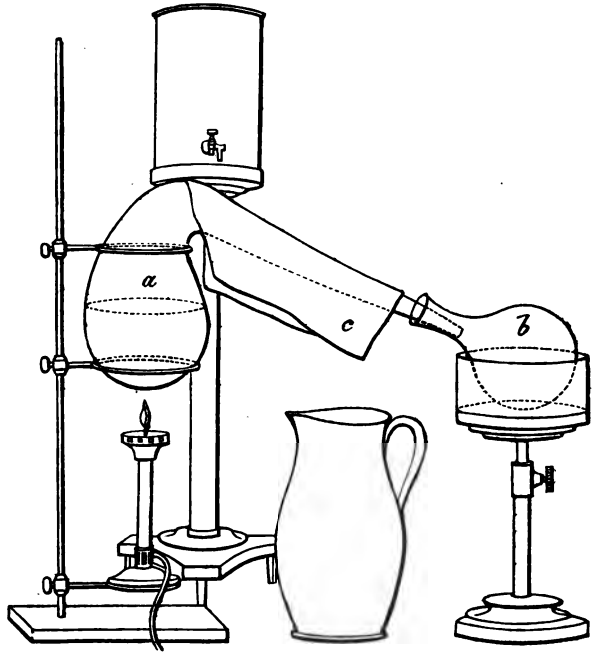
**48.** Nitrogen can be made to combine with oxygen, by mixing it with a large quantity of hydrogen, and burning the mixture. Electrical sparks passed through moist air also cause the formation of compounds of nitrogen, oxygen, and hydrogen, but both of these processes are too slow and costly for the preparation of large quantities of the compounds.

Five compounds of nitrogen with oxygen are known, viz. those represented by the formulae—

$N^2 O^5$ Nitric acid.
$N^2 O^4$ Nitric peroxide.
$N^2 O^3$ Nitrous acid.
N O Nitric oxide.
$N^2 O$ Nitrous oxide, or laughing-gas.

Compounds of nitric acid are formed spontaneously by the contact of air with decomposing animal or vegetable matter containing nitrogen, in presence of bases. It is necessary that some base, such as lime, or potash, or soda, be present, to combine with the acid in proportion as it forms.

**49.** A potassium or sodium salt of the acid is generally used for the preparation of the hydrogen salt, usually called **Nitric Acid.** Potassic nitrate, or saltpetre, as it is popularly termed, is generally used for preparing hydric nitrate on a small scale. The salt is mixed with an equal weight of strong sulphuric acid, and distilled in a retort until the contents of the retort fuse tranquilly, without giving off any more red fumes or condensable vapour. The yellow liquid which collects in the receiver has a density approaching to 1.5. It emits dense white fumes when brought in contact




Preparation of Hydric Nitrate.—*a* Retort containing potassic nitrate and hydric sulphate; *b* receiver to collect distilled nitrate; *c* wet bibulous paper.

with moist air, by combining with the moisture of the air to form a compound less volatile than the original acid or water. Even when mixed with large quantities of water the acid compound imparts a bright red colour to blue litmus-paper, and the original blue colour is restored by immersion in a solution of potash, or of soda, or lime, or any other substance possessing in a sufficiently strong degree the property of reversing the effect produced by an acid. When the acid is poured into a solution of potash, intense heat is

evolved, and if a good deal of water were not present with the substances, so great an elevation of temperature would be produced as to cause the mixture to boil, when the two opposite liquids come in contact with one another. By using dilute potash, and examining the liquid by litmus-paper after each addition, it is possible to destroy the power of blueing red litmus which the potash possessed, without imparting to the liquid the acid property of reddening blue litmus. The liquid is then termed neutral, and the compound of nitric acid with potassium which it contains is called potassic nitrate. It is the very salt from which our acid was prepared by the action of sulphuric acid.

In order to explain the process by which hydric nitrate is prepared it is best to compare the composition of the materials used in the process with the composition of the products finally obtained.

Oil of vitriol (hydric sulphate) is represented by the formula $SO^4H^2$; S being 32 parts by weight of sulphur, O being 16 parts by weight of oxygen; and accordingly $O^4$ being 64 parts by weight, and $H^2$ being 2 parts by weight of hydrogen. Potassic nitrate has the formula $NO^3K$, N being 14 parts by weight of nitrogen, and K 39 parts by weight of potassium. When the operation is complete, the fused mass in the retort, called hydro-potassic sulphate, has the composition $SO^4HK$; so that it is the same thing as hydric sulphate, from which one part by weight of hydrogen is taken away, and to which 39 parts by weight of potassium are added. The hydric nitrate collected in the receiver has a composition represented by the formula $NO^3H$, so that it is formed from potassic nitrate by removing K and putting in H.

The following equation

$$SO^4H^2 + NO^3K = SO^4HK + NO^3H$$

describes the process in its simplest form, as an interchange

of K in nitre for H in oil of vitriol. It generally happens that the oil of vitriol contains a little water mixed with it, and this water goes over with the nitric acid. Some of the hydric nitrate, moreover, decomposes, giving off oxygen-gas, and forming nitrous acid, a volatile compound of a yellowish red colour, which is generally seen in the distilling vessel, and which condenses in part with the acid in the receiver. By adding together the weight of sulphur, oxygen, and hydrogen indicated by the formula of hydric sulphate we have 98 as the weight of $S O^4 H^2$, and in like manner 101 as the weight of $N O^3 K$. The proportions represented by the formula are thus seen to be very nearly those of the experiment.

The hydric nitrate is an exceedingly acid salt, and is usually called nitric acid for brevity; but the hydrogen contained in it acts the part of basic metal, and being endowed with very feeble basic properties leaves the compound acid.

**50.** Hydric nitrate gives up a part of its oxygen with great facility to substances capable of combining with oxygen. When diluted with water its action is, however, less energetic than in the concentrated state, and by mixing it with oil of vitriol (a substance which tends to take water away from other compounds), the action of the nitrate is rendered even more violent than it is by itself.

Metallic copper thrown into dilute nitric acid of density 1.2 rapidly dissolves in it, while deep red fumes are given off in torrents; and if the experiment be performed in a vessel from which all atmospheric air has been previously removed, a colourless gas called nitric oxide is given off. The solution left at the end of the operation contains cupric nitrate, and the changes which take place in the process are represented by the equation

$$(H N O^3)^8 + Cu^3 = N^2 O^2 + [Cu (N O^3)^2]^3 + (H^2 O)^4.$$

This reaction affords a very good means of detecting

nitric acid when it occurs in the free state or in combination with a base. In the latter case strong sulphuric acid should be added to the liquid so as to combine with the strong base, and if much water be present sulphuric acid may be added in still greater quantity. The nitric oxide which comes off is easily recognized by the red fumes which it forms by contact with atmospheric oxygen.

Nitric acid is also detected by pouring a solution of ferric sulphate into a mixture of equal volumes of strong sulphuric acid and the solution containing the dilute nitrate. A brown colour shews itself immediately in the ferrous sulphate, if the quantity of nitric acid present be considerable, or after some time if only a trace of the acid be present.

Metallic zinc dissolves in dilute nitric acid even more readily than metallic copper, and a part of the nitric acid is reduced to nitrous oxide ($N^2O$). By using the acid still more dilute, some of it is not only deprived of all its oxygen but combined with hydrogen at the same time. This transformation of nitric acid into ammonia is complete when the acid is reduced by metallic zinc in presence of metallic iron, in a great excess of caustic potash.

**51.** Nitric acid reacts on potash only in one proportion, and from this circumstance it is termed a monobasic acid. The process, when hydric nitrate combines with potassic hydrate, consists in a replacement of the hydrogen of the acid salt by potassium, in the proportion represented by the symbol of that element (K); and the hydrogen which leaves the acid takes the place of the metal, forming water according to the equation $NO^3H + HKO = NO^3K + H^2O$. The process is therefore an interchange of metals (H and K) between two salts, forming two new compounds which are nearly neutral. The weights of these substances are $NO^3H = 63$, and $HKO = 56$; and the equation states that hydric nitrate and potassic hydrate react on one another in the

proportion of 63 parts of the acid salt to 56 of the basic salt. That they react on one another in no other proportion can be proved by bringing the substances together in other proportions, on each side of this one—that is, with a greater proportion of base to the acid, so as to see if the acid can combine with more base; and then with a greater proportion of acid to the potash, in order to ascertain whether the base can combine with more acid, or the acid with less base. When an excess of potash is used the mixture is found to be alkaline to test-paper; and if a part of the water be carefully driven off from it by evaporation, the solution deposits crystals of nitre of the same composition as if no excess of potash had been present at their formation, and the excess of potash remains uncombined in the liquid from which the crystals have been deposited, or what is called the mother liquid. By using an excess of nitric acid to the potash, a perfectly similar result is obtained in an even more striking manner, for not only does the excess of acid remain uncombined with the potassic nitrate, but it can be distilled off from the salt and recovered unchanged.

It is thus proved that nitric acid and potash combine in no other proportion than that represented by our equation.

Anhydrous nitric acid ($N^2O^5$) has not been obtained by removal of water from the hydrogen salt. It is prepared by passing chlorine gas over argentic nitrate, and condensing the products in a receiver cooled to a very low temperature. It is a solid crystalline compound, possessing the composition $N^2O^5$. When brought in contact with water it combines, with evolution of heat, to form hydric nitrate according to the equation $N^2O^5 + H^2O = (NO^3H)^2$. When kept in a closed tube it has been found to explode with violence, and without any external aid.

**52. Nitric Peroxide** ($N^2O^4$) is most conveniently obtained by heating plumbic nitrate in a stone-ware retort, and con-

densing in a cold receiver the red fumes which escape. The process consists in a breaking-up of the salt into plumbic oxide, which remains in the retort, and nitric peroxide and oxygen which pass off—

$$Pb\,N^2O^6 = Pb\,O + N^2O^4 + O.$$

The peroxide is at the ordinary atmospheric temperature a yellowish red liquid, but when cooled a few degrees below 0°C it becomes colourless. In contact with water it is decomposed, forming nitric acid and a lower oxide of nitrogen. It does not appear to combine with bases. When evaporated by the aid of heat in the pure state its vapour has a density corresponding to $N^2O^4 = 4$ vols. But when evaporated at a lower temperature by the aid of air it approaches a density corresponding to $N^2O^4 = 2$ vols.

**53. Hydric Nitrite** ($HNO^2$) is a very unstable compound, and is but little known even in its compounds. The red colour of nitric acid which has been exposed to the action of light is owing to the presence of nitrous acid. It is decomposed by water, forming nitrate, nitric oxide, and water. In its compounds it has much resemblance to nitrates. It is easily obtained by heating starch with a large quantity of nitric acid of density 1.25.

Anhydrous nitrous acid ($N^2O^3$) is formed by mixing nitric oxide ($N^2O^2$) with free oxygen, in the proportion of not more than one-fourth of its volume. The red vapour which is formed does not condense at 0°C, but if the vessel containing it be cooled to a temperature of about −20°C the acid condenses to a deep blue liquid.

**54. Nitric Oxide** ($N^2O^2 = 4$ vols.) is most conveniently prepared by dissolving copper in nitric acid of density 1.2 to 1.3. Its molecule ($N^2O^2$) occupies four volumes, the same as that occupied by a mixture of nitrogen and oxygen in these quantities. Its density is therefore 15. The gas has not been condensed to a liquid, by the greatest pressure and cold

hitherto applied to it. Nitric oxide does not support the combustion of a piece of wood; but more powerful combustibles, such as phosphorus or charcoal, burn very rapidly if kindled and then plunged into the gas. It combines with anhydrous sulphuric acid.

When two volumes of nitric oxide are mixed with not less than five volumes of hydrogen, and passed through a red-hot tube containing spongy metallic platinum, it is transformed into ammonia and water.

**55. Nitrous Oxide**, or laughing-gas ($N^2O = 2$ vols.), is most readily prepared by gently heating ammonia nitrate. Water and nitrous oxide are the only products, and the decomposition takes place according to the equation

$$N^2O^3H^4 = N^2O + 2\,(H^2O).$$

The gas dissolves in water at 0°C to the extent of 1.3 of its volume, and at 15°C water dissolves more than two-thirds of its volume. It is therefore customary to collect the gas by displacement of hot water in the pneumatic trough. It may also be collected by displacement of air, if led to the bottom of a jar full of air, as it is about half as heavy again as air. Its exact density is 22.

Nitrous oxide is a colourless gas, devoid of odour; but it produces when inhaled inebriating effects, which have gained for it the trivial name of laughing-gas. It supports the combustion of most substances with an intensity so nearly equal to that of oxygen that it might be mistaken for that gas, if carelessly examined. A kindled splint bursts into flame in nitrous oxide as in oxygen. Phosphorus burns with dazzling splendour in nitrous oxide, and affords an exceedingly convenient means of distinguishing the gas from oxygen, as nitrogen is liberated by the phosphorus, in volume equal to the nitrous oxide employed. Nitric oxide does not produce red fumes when mixed with nitrous oxide. Potassic pyrogallate does not absorb nitrous oxide as it does

oxygen. Nitrous oxide can be condensed into a liquid at the temperature of 0°C by a pressure of about 36 atmospheres, and the liquid nitrous oxide is one of the most powerful cooling agents known. When some of the liquid is removed from the vessel in which it was formed by pressure, and brought out into an open vessel, it boils with great violence, and the portion which evaporates absorbs so much heat, that the remaining liquid is cooled to a temperature of about −88°C, at which it boils under the common atmospheric pressure.

A still lower temperature is obtained by placing this liquid in a vacuum, maintained by a powerful air-pump, and the accelerated evaporation which takes place at that greatly reduced pressure, serves to freeze some of the nitrous oxide into a transparent solid like ice.

The coefficient of expansion of nitrous oxide gas is very slightly greater than that of oxygen. The specific heat of the gas is .2238. The specific heat of a mixture of oxygen and nitrogen in the same proportions is .2284.

## APPENDIX TO CHAPTER VII.

### PROBLEMS.

45. What weight of hydric nitrate $HNO^3$ ought to be obtained from one kilogramme of sodic nitrate $NaNO^3$, supposing none of the product to be decomposed?

46. How much hydric sulphate is required for the decomposition of 500 grammes of potassic nitrate, according to the equation $H^2SO^4 + (KNO^3)^2 = K^2SO^4 + (HNO^3)^2$?

47. Ten grammes of nitric oxide are required; what weight of the materials would you require for their formation?

48. What weight of water is formed by the reaction of 200 grammes of hydric nitrate upon potassic hydrate, according to the equation

$$HNO^3 + HKO = HNO^3 + H^2O.$$

49. 300 grammes of pure hydric nitrate are mixed with 800 grammes of potassic hydrate. How much more of the nitrate must be added in order to render the mixture neutral?

50. What weight of oxygen is liberated by the gradual action of heat in 300 grammes of plumbic nitrate?

51. What volume of nitric oxide is required for the combustion of ten cubic centimeters of hydrogen? and what will be the volume of the nitrogen liberated?

52. What volume of oxygen is needed for the conversion of ten grammes of nitric oxide (in presence of water) into hydric nitrate?

53. What weight of nitrous oxide is obtained from a kilogramme of ammonia nitrate? and what is the volume of the gas at the normal temperature and pressure?

54. What volumes of the free gases would you obtain by the decomposition of a liter of nitrous oxide?

55. What volume of hydrogen could be burnt by ten grammes of nitrous oxide?

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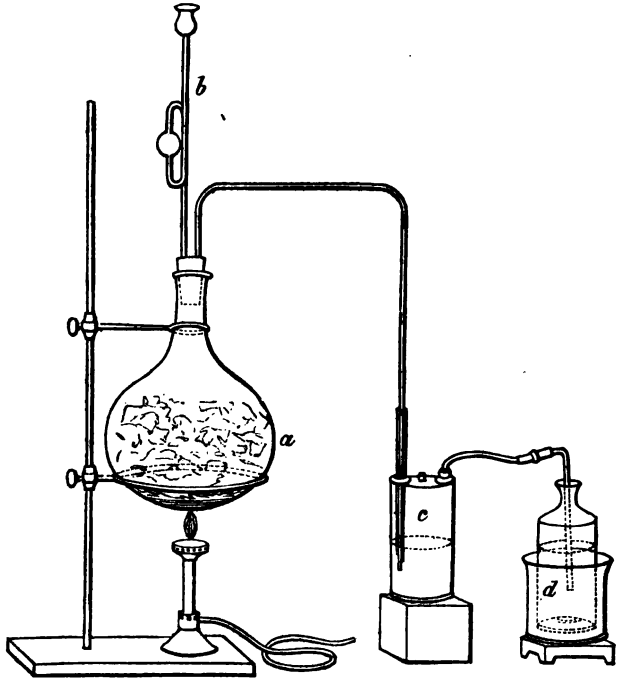
## CHAPTER VIII.

**56. Ammonia** ($NH^3$) is a minor constituent of the atmosphere, and is given off by putrifying animal and vegetable substances containing nitrogen. It is also one of the products of the decomposition of coals by heat, and is collected in large quantities at gas-works. It is usually obtained by the action of lime on sal-ammonia. The lime should be previously slaked, that is combined with water, and the light powder thus obtained is mixed with about two-thirds of its weight of finely-powdered sal-ammonia, and the mixture is heated in a flask similar to that used for evolving oxygen, fitted however

with a wash-bottle to wash the gas. The sal-ammonia is a compound of ammonia with hydrochloric acid, and the lime takes the hydrochloric acid from it, whilst ammonia is liberated, together with the water from the lime.

The reaction is thus described by an equation:

$$(N H^4 Cl)^2 + Ca H^2 O^2 = (N H^3)^2 + Ca Cl^2 + (H^2 O)^2.$$




Preparation of ammonia solution.—*a* Flask containing sal-ammonia and lime; *b* safety tube; *c* wash-bottle; *d* bottle containing distilled water to be saturated.

The ammonia is usually led into water, and the solution thus obtained goes commonly by the name of ammonia. The gas itself can be collected by displacement of mercury,

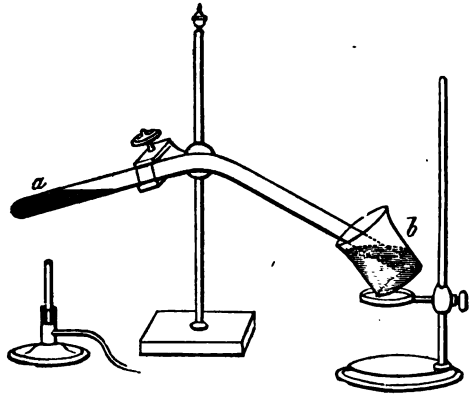
or for some purposes it might be collected like hydrogen, by displacement of air, by leading it up to the top of a bottle suspended mouth downwards. Its density is 8.5. If required free from moisture it should be passed through a tube containing powdered potassic hydrate. Ammonia is remarkable for its pungent smell, and it exerts so powerful a corrosive action on moist animal tissues that the most serious consequences might arise from inhaling any considerable quantity of it. A piece of red litmus-paper immediately turns blue by contact with ammonia, and nitric acid is neutralised by ammonia as effectually as by potash itself, so that ammonia is justly entitled to the name which is frequently given to it, of volatile alcali. When a glass rod, moistened by nitric acid of such strength as not to fume in the air, is brought in contact with ammonia, dense white fumes are formed, owing to the formation of solid ammonia nitrate in the air, by contact of the vapour of nitric acid with the volatile alcali.

Ammonia burns with the greatest difficulty; but when mixed with oxygen it can be exploded, and if sufficient oxygen be present ammonia nitrate is formed by the explosion. A gradual oxidation of ammonia, forming nitrous acid, takes place at the common atmospheric temperature, in presence of finely divided metallic copper.

When passed through a red-hot tube ammonia is decomposed, and the same result can be obtained by passing a succession of electric sparks through ammonia gas confined in a glass tube over mercury. The mixture of nitrogen and hydrogen formed by the decomposition of ammonia occupies exactly double the volume of the compound of the two gases. The expansion of ammonia gas by heat takes place very nearly in the same proportion as that of oxygen, hydrogen, and nitrogen, the coefficient of expansion of ammonia being slightly greater than that of the permanent gases. The

specific heat of ammonia is .5083, which is considerably less than the nitrogen and hydrogen contained in it possess in the uncombined state. The specific heat of a mixture of hydrogen and nitrogen in the proportions in which these gases are contained in ammonia is .802.

**57.** Ammonia can be condensed into a liquid of about 0.76 density, by passing the gas slowly into a tube cooled by a powerful frigorific mixture below the temperature of −38.5, at which liquid ammonia boils at the ordinary atmospheric pressure. At the temperature of 10°C it requires a pressure of about 6 atmospheres for its liquefaction. The easiest way to prepare this liquid on a small scale is to saturate some dry argentic chloride with ammonia gas, and to put




Preparation of liquid ammonia.—*a* Heated end of tube containing compound of silver-chloride and ammonia; *b* cooled end of tube where liquid ammonia collects.

the compound into a strong glass tube, sealed up at one end and bent in the middle at an angle of about 120°. The tube is then sealed up at the other end, by the aid of a blow-pipe flame, and when cold is ready for use. If the empty end of

the tube be surrounded by ice, whilst the end containing the compound of ammonia and chloride is heated by means of a water bath, the ammonia is gradually expelled from the compound and is confined by the narrow dimensions of the tube at so great a pressure that a considerable proportion of it condenses in the cold end of the tube. Liquid ammonia solidifies at about $-90°C$. A solution of ammonia in water saturated with the gas at a low temperature g ves off a large part of the gas when heated, and a strong solution of ammonia can therefore be used for the preparation of liquid ammonia. The operation is performed in iron vessels from which all atmospheric air has been removed, and if the water from which ammonia has been expelled by heat be cooled again, it condenses the ammonia gas above it, and causes an evaporation of the liquid ammonia which has been previously condensed. The evaporation of this liquid ammonia serves to freeze water outside the vessel.

**58.** Ammonia dissolves in water with great rapidity, and gives off a considerable quantity of heat in the process. At 0°C water takes up more than a thousand times its volume of the gas, at 15°C upwards of 700 volumes, and at 24° nearly 600. The solutions smell strongly of ammonia, and when saturated give off a part of the gas with extreme readiness. Their density is less than that of water, and the strongest solutions have the smallest density. Quantitative determinations have been made of the proportion of ammonia and water, in solutions of various densities, and the results of these determinations are recorded in tables, which should be consulted whenever it is wanted to know the strength of a solution of which the density has been ascertained. One of these tables will be found at the end of the volume.

Ammonia, when dissolved in water, must be considered to be in combination with one molecule of water, in the form of the compound $NH^5O$. On the combination of aqueous

ammonia with nitric acid, forming ammonia nitrate, there is a process perfectly similar to that which occurs when aqueous potash combines with the acid; but in order to see the resemblance, we must arrange the elements of the compound of ammonia and water, so as to shew its analogy with the potassic hydrate HKO. For that purpose we can write it $H(NH^4)O$, so that the group of elements $NH^4$ is contained in the aqueous ammonia instead of the element K in the potassic hydrate. We have then to represent the combination of nitric acid by the following equation, viz.

$$NO^3H + H(NH^4)O = NO^3(NH^4) + H^2O;$$

just like

$$NO^3H + HKO = NO^3K + H^2O.$$

The action of solution of ammonia on compounds of nitric acid with weak bases is very similar to the above. Thus with argentic nitrate the following reaction takes place:

$$NO^3Ag + H(NH^4)O = NO^3(NH^4) + HAgO.$$

The alcalies and alcaline earths are stronger bases than ammonia, and are not separated from acids by it.

**59.** It will be seen by the further study of ammonia that it combines with nearly all acids with which potash is capable of combining, and that $NH^4$ plays the same part in the salts of ammonia which K plays in the salts of potassium. In fact this group of elements ($NH^4$) is in its compounds like the metal potassium. For these reasons it is found convenient to give to this group of elements a name bearing some resemblance to the names of metals, and the object is obtained by calling it ammonium. Ammonium is at present only known in compounds, as it always decomposes into ammonia and hydrogen as soon as it is turned out of combination. The nearest approach to free ammonium is a compound of mercury with it, a substance in which the metal mercury is united with the compound metal ammonium so feebly that the properties of the constituents are less altered than in firmer

compounds. The compound is easily obtained by putting sodium amalgam into a strong solution of sal-ammonia. The sodium rapidly dissolves, taking the chlorine from the ammonium, while the ammonium combines with the mercury. A soft buttery mass is thus obtained, occupying an enormous volume compared with that of the original mercury—

$$Na\,Hg^n + N\,H^4Cl = N\,H^4H\,G^n + Na\,Cl.$$

The ammonium amalgam very rapidly decomposes when removed from the liquid, and gives off a mixture of two volumes of ammonia to one volume of hydrogen.

**60.** Ammonia nitrate (empirical formula $N^2O^3H^4$, rational formula $NO^3NH^4$) is easily prepared by dissolving ammonia carbonate in nitric acid, and evaporating the solution till it crystallizes. The salt is then deposited in the shape of needle-shaped crystals, which can be dried on bibulous paper. Ammonia nitrate dissolves in water very rapidly, and in very large quantity. Its liquefaction absorbs a considerable quantity of heat, which is evolved again when the salt crystallizes out from its solution. The salt is frequently used for producing a low temperature for the formation of ice, and is recovered again after use by evaporation of its solution. When thrown on to red-hot coals the salt explodes, but when heated gradually by means of a lamp it decomposes entirely into nitrous oxide and ammonia.

Ammonia nitrate ($N^2H^4O^2$ or $NO^4(NH^4)$) is a very unstable salt. It can be obtained by decomposing plumbic nitrite by ammonia sulphate. The solution decomposes when heated, giving off nitrogen gas. A solution of ammonia precipitates a solution of cupric sulphate, but when added in greater quantity it dissolves the precipitate, forming a deep azure blue solution. Ammonia chloride forms with platinic chloride a compound very slightly soluble in water, and insoluble in alcohol. It possesses the composition $Pt(NH^4)^2Cl^6$. The most delicate test for ammonia is

Nessler's test, viz. potassic iodide saturated with mercuric iodide. When mixed with an excess of potash, this solution gives a reddish yellow precipitate with a liquid containing the least trace of ammonia.

## APPENDIX TO CHAPTER VIII.

### PROBLEMS.

56. What will be the dimensions of a flask capable of containing 20 grammes of ammonia gas, at 12°C and 730 mm. pressure?

57. What weight of sal-ammonia must be taken to obtain one kilogramme of ammonia?

58. What volume of nitrogen is obtained by the combustion of 10 cubic centimeters of ammonia?

59. What volume of nitrogen will be evolved by the action of nitrous acid in 10 grammes of ammonia?

60. 100 grammes of nitre ($KNO^3$) are distilled with hydric sulphate. What weight of ammonia will be required to neutralize the distillate? and what will be the weight of the nitrate formed?

61. Three grammes of nitric oxide are mixed with an excess of hydrogen and passed over moderately heated platinum sponge. What weight of ammonia is formed?

62. 2.14 grammes of ammonia chloride ($NH^4Cl$) were obtained by the action of metallic zinc in presence of iron on a mixture of a nitrate with potash solution. What weight of anhydrous nitric acid was required for its formation?

63. A weighed quantity of an organic substance containing nitrogen was heated with soda-lime, and the ammonia was passed into hydrochloric acid and combined with platinic chloride. 3.428 grammes of the double chloride were thus obtained. How much nitrogen is contained in this?

# CHAPTER IX.

**61. Carbon** occurs as diamond, plumbago, charcoal, &c. It is remarkable for the great difference between the properties which it possesses in these different substances, differences which are not owing to the presence of any foreign substance in any of these varieties of carbon, but which belong to the carbon itself. Diamonds have a density of about 3.55, whilst plumbago has only a density of about 2.2. Diamond is the hardest known substance, whereas plumbago is so soft, that even paper rubs off particles from it. Diamond is transparent, plumbago is opaque. Diamond is a very bad conductor of electricity, and usually ranks among non-conductors. Plumbago, on the contrary, conducts well, and equals some metals in this respect. Diamond crystallizes in octohedral forms, or in forms nearly related to them, plumbago crystallizes in six-sided plates. The specific heat of diamond is .14687, while that of plumbago is .2008, and that of charcoal .2415. The two substances are so entirely different in all their properties that they could not be classed together at all, were it not for the fact that both of them can be made to combine with oxygen, and, once combined, retain no traces of the original differences between them, for carbonic acid made from diamonds is identical with carbonic acid made from plumbago. At a very high temperature, such as that obtained by discharging a powerful galvanic battery between two carbon points, diamonds swell up, become opaque, and are transformed into a material nearly resembling plumbago. The inverse transformation has not yet been effected.

Plumbago, or black-lead, as it is commonly but very improperly called, is obtained from mines in Cumberland,

Ceylon, and some other districts. A very similar substance is formed by the gradual cooling of large masses of cast iron. The molten mass contains carbon in solution, and a part of this carbon crystallizes out on the surface of the iron while it is cooling. A very pure and dense variety of carbon is found in the roof of old gas-retorts, where it had been gradually deposited, by the action of the high temperature upon the coal gas which was passing out.

**62. Coke** is a dense variety of carbon, prepared by heating coals to a bright red heat, and thereby expelling, as gas, oils, &c., all the hydrogen and oxygen of the native coal, with some of its carbon. Coals which are rich in compounds of hydrogen become semi-fluid before decomposition, and the coke which is left from them is in large coherent masses. Such coals are called caking coals. Welch coal and anthracite contain less hydrogen, and burn with very little flame or smoke. They approach more nearly to the composition of coke than the bituminous coals. Coke generally contains earthy matter, which remains as an ash when the carbon is burnt away, and sometimes a good deal of sulphur in the form of per-ferric sulphide or pyrites, which diminishes its value considerably for foundry use. Charcoal is the name given to the carbon obtained by expelling all the hydrogen and oxygen from wood by heat, the necessary heat being usually obtained by burning some of the wood. The ashes of charcoal contain potassic carbonate. Few persons can have used coke or charcoal for fuel without noticing the comparative difficulty of lighting coke, inasmuch as those parts of it to which heat is applied allow the heat to escape from them into the rest of the heap far more rapidly than is the case with charcoal. This superior conducting power for heat which belongs to coke is mainly owing to the comparatively dense state of aggregation of its particles, acquired by the high temperature to which they have been exposed; for if a piece of

soft porous charcoal be heated to a good white heat in a closed vessel it is found to become harder and more difficult of ignition than before, in fact very much like coke itself. At no temperature to which it has been exposed does carbon evaporate, or even shew signs of fusion.

**63.** When prepared at a comparatively low temperature charcoal possesses the power of condensing large quantities of gas on its surface, and the gas so condensed is capable of producing effects which it cannot produce under similar circumstances when uncondensed. Thus, the oxygen of atmospheric air when condensed by charcoal combines rapidly with all volatile combustible bodies which come in contact with it. Many of the most dangerous impurities in atmospheric air, such as the fetid products given off by putrefying animal or vegetable matter, can be removed from it completely by a process of total oxidation, by passing the impure air through a sufficient thickness of powdered charcoal. The air is thus rendered inodorous and harmless. Respirators have been constructed by Dr. Stenhouse for purifying in this manner the air which passes into the lungs, and their efficacy is increased by a small quantity of finely-divided platinum spread over the charcoal. It is much to be regretted that this most valuable safeguard to health is not more generally known and adopted.

Animal charcoal, bone black, ivory black, &c., are names given to mixtures of carbon with calcic phosphate, obtained by heating bones in a closed vessel until the organic matter contained in them is completely decomposed, leaving charcoal intimately mixed with the incombustible materials of the bones. The presence of the phosphate in this animal charcoal enables the carbon to remove various colouring matters from liquids, and the substance is accordingly much used by sugar-refiners and others for the purpose of decolourizing solutions. An exceedingly striking illustration of the action

of animal charcoal is obtained by putting some of it, in the form of a fine powder, into water coloured deep blue by sulphindigotic acid. The colouring matter is speedily absorbed by the animal charcoal, and a colourless liquid is obtained by filtration. The charcoal obtained by calcining blood with potassic carbonate is found very efficacious for some purposes of decolorization.

Lamp-black is a fine powder of charcoal, usually contaminated by oily matter. It is made by burning hydro-carbons, such as turpentine, with a supply of air insufficient for their complete combustion. The smoke from these flames, or better still, from very bituminous coal, is made to pass through long horizontal flues, where the lamp-black gradually collects. Lamp-black, when mixed with linseed-oil and soap, forms printing-ink.

**64.** When heated to redness in contact with free oxygen carbon burns, forming carbonic acid. Dumas found that by burning diamonds in oxygen gas, 44 parts by weight of carbonic acid are formed for every 12 parts by weight of carbon. The compound is therefore represented by the formula $CO^2$.

When heated in carbonic acid, carbon also burns at the expense of the oxygen of that compound, $C + CO^2 = 2(CO)$; and when air passes up through a thick layer of red-hot charcoal or coal there is a formation of carbonic acid at the bottom, but this carbonic acid in passing over the red-hot charcoal takes up carbon, and becomes reduced to carbonic oxide.

At very high temperatures carbon combines also with hydrogen, forming the gaseous compound $C^2H^2$, called acetylene. This is obtained by discharging a powerful galvanic battery by carbon points, separated from one another by an atmosphere of hydrogen. With nitrogen, carbon does not combine without the intervention of other substances.

Steam at high temperatures is reduced by red-hot charcoal, according to the equation—

$$C + H^2O = CO + H^2.$$

At a red heat carbonic acid is formed, as well as carbonic oxide.

Ammonia is also decomposed by charcoal at a red heat. The products of the action are free nitrogen, hydrogen, and ammonia cyanide ($CN^2H^3$). Charcoal evolves 8,080° of heat on burning to form carbonic acid. Only two compounds of carbon and oxygen are known, viz. carbonic acid and carbonic oxide.

**65. Carbonic Acid** gas is prepared by dissolving chalk or white marble in hydrochloric acid—

$$CaCO^3 + 2(HCl) = CaCl^2 + H^2O + CO^2.$$

Sulphuric acid is used instead of hydrochloric acid, if carbonic acid be required for purposes in which the presence of a little arsenic would be injurious.

The gas is about half as heavy again as atmospheric air; its density being like that of nitrous oxide, 22, $Co^2 = 2$ vols. It neither burns nor supports combustion, so that a lighted taper is extinguished when lowered into carbonic acid gas. It can be poured from one vessel to another by displacement of air, but should not be left long in an open vessel, as it gradually escapes by diffusion. Clear lime-water is precipitated by carbonic acid, the precipitate being calcic carbonate.

When subjected to a pressure of 35.4 atmospheres, at the temperature of 0°C, carbonic acid is condensed into a liquid. At −25°C it only requires 17.2 atmospheres pressure for its condensation. The liquid carbonic acid is frequently prepared by putting hydro-sodic carbonate (often called bicarbonate of soda) and water into a strong wrought-iron bottle, together with a narrow pot nearly full of sulphuric acid. The bottle is closed by a screw-plug, and then agitated so as

to shake the acid out of its pot, and bring it in contact with the carbonate.

Liquid carbonic acid is said to have a density of 0.9 at $-20°C$, and a density of 0.6 at 30°; so that a rise of temperature of 50° increases its volume about 50 per cent., or about three times as much as if it were a gas. The liquid acid is usually distilled out into another vessel before use. When brought out to the open air a portion of the carbonic acid boils so rapidly as to freeze the remainder into a white solid, looking very much like snow. An alcohol thermometer immersed in this solid carbonic acid falls to $-78°C$. The solid dissolves readily in ether, and can be most conveniently used in that form for freezing purposes. Metallic mercury is instantly frozen into a solid mass like lead by contact with the solution; and if it comes in contact with the skin, a blister is said to be produced very similar to that produced by a burn.

The solid acid can, however, be taken up by the hand without producing any painful sensation, as it does not come in contact with the surface of the hand sufficiently to absorb much heat from it. The specific heat of gaseous carbonic acid, between 10° and 200°C, is .2169. At the ordinary atmospheric temperature of 15°C water dissolves about its own volume of carbonic acid, and the solution has a slightly acid reaction to litmus-paper. At 0°C the exact volume of carbonic acid absorbed by water is 1.7967; at 10°C it is 1.1847; at 20°C it is 0.9014. A piece of litmus, reddened by the solution of carbonic acid, resumes its blue colour by a few minutes' exposure to the air, by evaporation of the acid. The aqueous solution no doubt contains hydric carbonate ($CO^3H^2$), although that compound has never been separated from the water.

**66.** Carbonic acid reacts in two distinct proportions upon potash, forming a normal carbonate called potassic carbonate

($C O^3 K^2$) and a double salt hydro-potassic carbonate often called bicarbonate of potash ($C O^3 H K$). The former salt is decidedly alkaline in its reation and properties, proving that carbonic acid is by no means capable of neutralizing two molecules of potash. Even the second salt is slightly alkaline. Ammonia combines with carbonic acid, forming a solid and very volatile compound, well known by the name of volatile salt of hartshorn.

In the pure state the commercial salt has the composition $2((N H^4)^2 O) 3 (C O^2)$, and is called ammonia sesqui-carbonate.

## APPENDIX TO CHAPTER IX.

### PROBLEMS.

64. What weight of air is needed for the complete combustion of one kilogramme of carbon?

65. A chamber contains 60 cubic meters of air at 14°C and 760 mm. pressure. 500 grammes of carbon are completely burnt in the room and nothing allowed to escape. What is the per centage composition of the residual mixture, assuming the original air to have consisted of 21 per cent. oxygen and 79 per cent. nitrogen by volume?

66. What weight of hydro-sodic carbonate, and what weight of hydric sulphate, must be used in order to evolve one kilogramme of carbonic acid according to the equation—

$$H Na C O^3 + H^2 S O^4 = H Na S O^4 + H^2 O + C O^2 ?$$

67. What volume of carbonic acid would be obtained by combining 100 grammes oxygen in the proper proportion with carbon?

68. What weight of carbon is contained in a litre of carbonic acid?

69. What weight of calcic carbonate must be dissolved for the evolution of 20 litres of carbonic acid at 15°C and 760 mm. pressure?

# CHAPTER X.

**67. Carbonic Oxide** (C O) is most conveniently prepared in large quantities by passing dry carbonic acid through a red-hot tube containing charcoal. In most cases it is best made by mixing potassic formiate with sulphuric acid, in sufficient quantity to form a thin mud, and heating the mixture. The reaction which ensues is this—

$$CHKO^2 + SO^4H^2 = CO + SO^4HK + H^2O.$$

Carbonic oxide is a little lighter than atmospheric air; its density being 14, the same as that of nitrogen. It burns in air with a pale blue flame, forming carbonic acid, and every two volumes of carbonic oxide combine with one volume of oxygen to form two volumes of carbonic acid. When the mixture in these proportions is fired by the electric spark it explodes with force about equal to that of the explosion of oxy-hydrogen gas. The heat of combustion of carbonic oxide is 2,403 degrees; and as 28 parts by weight of the gas contain 16 parts by weight of oxygen and 12 of carbon, it follows that one part by weight of carbon in carbonic oxide evolves 5,607 degrees of heat on taking up the additional oxygen to form carbonic acid. If this quantity of heat is deducted from 8,080 degrees, which charcoal gives off when it burns to carbonic acid, the difference, namely $8080 - 5607 = 2473$, shews how much heat is evolved by one part by weight of carbon burning to form carbonic oxide.

**68.** Some furnaces are occasionally to be seen at work under such conditions that the air, after forming carbonic acid with the fuel with which it first comes in contact, is then forced over red-hot coals, so as to reduce this carbonic acid

to carbonic oxide, which escapes unburnt: and the above calculation shews that in such cases there is less than one-third the total quantity of heat of combustion of the fuel given off. To rectify the working of such a furnace the mixture of nitrogen and carbonic oxide which passes out from the coals should be intimately mixed, while still hot, with as great a volume of air as that which passed through the coals. The weight of air needed for burning completely one kilogramme of coal is nearly 12 kilos., and these occupy at the common temperature about $9\frac{3}{4}$ cubic meters. To verify these numbers we should first calculate the weight of oxygen needed to burn a kilo. of coal, and then how much air must be taken in order to supply the needful quantity of oxygen. The formula $CO^2$ shews that for every 12 parts by weight of carbon 32 parts by weight of oxygen are needed, or for one of carbon $2\frac{2}{3}$ of oxygen. As air contains 23 per cent. of oxygen by weight, we have the proportion $23 : 100 = 2\frac{2}{3} : x$, whence 11.56 kilos. is the weight of air needed to burn one kilo. of carbon. Coals, however, usually contain some unburnt hydrogen, and this renders a greater proportion of oxygen necessary; so that 12 kilos. of air is by no means too much to allow. Allowing 1.293 kilo. as the weight of a cubic meter of air at 0°, or 1.2256 at 15°C, the proportion $1.2256 : 1 = 12 : x$ gives us 9.7584, or in round numbers $9\frac{3}{4}$, as the number of cubic meters of air at 15° weighing 12 kilos., needed for the combustion of one kilo. of coal.

**69.** The specific heat of carbonic oxide is .2450. When it combines with oxygen the carbonic acid formed would have a specific heat equal to .235 if it retained that of the oxygen and of the carbonic oxide without loss, whereas the specific heat of carbonic acid is only .2103. It has never been condensed by cold or pressure into a liquid. Carbonic oxide is stated to be poisonous when taken into the lungs for some time, and the deadly effects produced by a charcoal fire in an

unventilated room are attributed to its action. It is rather less soluble than oxygen in water. A solution of potash does not absorb it in the cold, but carbonic oxide is slowly but completely absorbed by semi-fluid potash at 100°C, producing potassic formiate—

$$CO + HKO = KCHO^2.$$

Carbonic oxide is absorbed by a solution of cuprous chloride ($Cu^2Cl^2$) in aqueous hydrochloric acid. Melted potassium also absorbs carbonic oxide.

**70.** Oxalic acid ($C^2O^3$) is not known in the free state. Its salts are contained in the juice of many plants, such as sorrel, lichens, &c. It is a compound intimately related to the oxides of $H^2$. Its compound with water (hydric oxalate, $H^2C^2O^4$), generally called oxalic acid, is now prepared on a large scale by heating sawdust with a mixture of potassic and sodic hydrate. The alkaline oxalates thus obtained are dissolved in water and boiled with milk of lime. The lime carries down the acid as an insoluble salt, and the alkalies are left in solution ready for using with some fresh sawdust as soon as they have been boiled down—

$$Na^2C^2O^4 + CaO^2H = (NaOH)^2 + CaCO^4.$$

The calcic oxalate is decomposed by dilute hydric sulphate—

$$CaC^2O^4 + H^2SO^4 = H^2C^2O^4 + CaSO^4.$$

Oxalic acid may easily be made on a small scale by the action of nitric acid on sugar or starch. Eight parts of nitric acid of 1.37 density are heated with one part of sugar, and the mixture evaporated is about ¼ of its original volume, when crystals of the hydrogen salt are deposited on cooling.

The crystals contain two molecules of water—

$$C^2H^2O^4(H^2O)^2,$$

which can be expelled by gentle heat, and a white powder is then left consisting of the hydrogen salt $H^2C^2O^4$.

When heated more strongly the acid decomposes chiefly

into carbonic acid and carbonic oxide, whilst water is liberated, $C^2H^2O^4 = CO^2 + CO + H^2O$; but a small quantity of the compound is carried up by the escaping gases, and condenses on any cold surface over which it is led, whilst a little formic acid is formed at the same time.

When an oxalate is heated with strong sulphuric acid it breaks up entirely into carbonic acid and carbonic oxide, whilst water is liberated—

$$C^2H^2O^4 = CO^2 + CO + H^2O.$$

When hydric oxalate is heated to a temperature of 100° with glycerine, it breaks up entirely into hydric formiate and carbonic acid—

$$C^2H^2O^4 = CO^2 + CH^2O^2.$$

**71.** Oxalic acid dissolves readily in water, and has an intensely acid taste, and acid reaction to litmus-paper. It expels carbonic acid from its salts, whilst water is formed at the same time, and destroys the alkaline reaction of potash and soda. With either of these bases it reacts in two distinct proportions, forming first a double salt of hydrogen and potassium—

$$H^2C^2O^4 + KOH = HKC^2O^4 + H^2O;$$

or, with twice as much base, it forms the normal potassic oxalate—

$$H^2C^2O^4 + (KOH)^2 = K^2C^2O^4 + (H^2O)^2.$$

There is also another double salt containing hydrogen and potassium, hydro-tri-potassic binoxalate, $HK^3C^4O^8$.

Ammonia combines with hydric oxalate to form either a neutral ammonia oxalate, $(NH^4)^2C^2O^4H^2O$, or hydro-ammonic oxalate, $H^2O\,H\,(NH^4)\,C^2O^4H^2O$.

The salts of oxalic acid, containing calcium, barium, or the heavy metals, such as zinc, iron, lead, &c., are insoluble in water but soluble in acids. One of the most important of its salts is the calcic oxalate $CaC^2O^4$, which is insoluble in water and in acetic acid, though soluble in hydrochloric

or in nitric acid. When the salt is cautiously heated it decomposes, leaving a colourless residue of calcic carbonate, whilst carbonic oxide escapes. The residue dissolves with effervescence in acetic acid. When mixed with manganic peroxide, in presence of hydrochloric acid, the oxalic acid in oxalates is completely oxidized to carbonic acid.

Commercial oxalic acid generally contains some mineral impurities, which are left as an ash when the acid is burnt. If it be required in a state of purity it should be made from distilled vinic oxalate, which is easily decomposed by water.

**72. Formic Acid** ($C^2H^2O^2$) is not known in the free state. Its hydrogen salt, $CHO^2$, was originally extracted from red ants, and was named from that source. It is formed by the partial oxidation of a great variety of organic bodies, such as sugar, gum, tartaric acid, alcohol, &c.; but by far the best way of making it is by the action of glycerine on dried oxalic acid. A tubulated retort is about one-quarter filled with concentrated glycerine, and as much dry oxalate thrown in as the glycerine can cover. The mouth of the retort is inserted into a flask receiver, and its body is surrounded by boiling water. Formic acid distils over into the receiver, whilst carbonic acid escapes; and when it ceases to come over some fresh oxalate is put into the retort, and the process is thus repeated with the same portion of glycerine until enough acid has been collected. If the compound be required free from uncombined water, it should be made by the action of sulphuretted hydrogen on dry plumbic formiate—

$$Pb(CHO^2)^2 + H^2S = PbS + (CH^2O^2)^2.$$

It is then obtained in a liquid of 1.235 density, and boiling at 100°.

Compounds of formic acid greatly resemble those of acetic acid (or vinegar) in their properties. One of the least soluble of the formiates is the plumbic salt. With

calcium it forms an exceedingly soluble salt, obtained by dissolving lime in hydric formiate—

$$Ca\,O + (H\,C\,H\,O^2)^2 = H^2\,O + Ca\,(C\,H\,O^2)^2.$$

Mercuric and argentic formiates are completely decomposed by heat in presence of water, the metal being reduced and carbonic acid making its escape in the effervescence. Formic acid resembles nitric acid in reacting on potash in one proportion only, forming the salt $K\,C\,H\,O^2$, containing one atom of potassium in the place of one atom of hydrogen in the hydrogen salt. This neutral salt forms an unstable compound with the acid hydrogen salt, having the composition $(K\,C\,H\,O^2)\,(H\,C\,H\,O^2)$; but this hydro-potassic formiate loses its hydrogen salt even at the heat of the water-bath.

There are many compounds of carbon and hydrogen, but only one of them (acetylene) has been made by the direct combination of the elements. Several hydro-carbons are gaseous, many are liquid, and some, as paraffine, are solids. The three simplest hydro-carbons will alone be described at present; and first of these marsh gas.

## APPENDIX TO CHAPTER X.

### PROBLEMS.

70. What volume of carbonic acid must be passed over white-hot charcoal for the preparation of 10 litres of carbonic oxide?

71. What volume of carbonic oxide will be obtained by passing a litre of oxygen over an excess of white-hot charcoal?

72. Ten litres of a mixture of carbonic oxide and oxygen,

in the combining proportions, are fired by the electric spark. What volume of carbonic acid is formed?

73. A ton of carbon has to be burnt to carbonic oxide by means of air. What volume of air is needed for the purpose? What will be the volume of the mixture formed? How much heat will be evolved in the process? How much heat will be obtained by burning the carbonic oxide?

74. What weight of water, supplied at 0°C, would be evaporated at atmospheric pressure by the total heat of combustion of one kilogramme of carbon?

75. How much heat is evolved by the combustion of a litre of carbonic oxide, measured at 0°C and 760 mm.

76. 50 grammes of crystallized oxalic acid are decomposed by sulphuric acid. What volume of carbonic oxide is evolved?

77. What weight of ammonia would be neutralized by a kilogramme of hydric oxalate ($H^2C^2O^4$)?

78. What weight of pure hydric formiate would be obtained from a kilogramme of hydric oxalate by the action of glycerine? and what weight of ammonia would this formiate neutralize?

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# CHAPTER XI.

**73. Marsh Gas** ($CH^4$). It is formed by the putrefaction of vegetable matter under water, and has thence obtained its name. It is also given off from the coal mines, and by mixing with air in the shafts and galleries gives rise to an

explosive mixture which it is the duty of the superintendent to remove by thorough ventilation, before it accumulates in sufficient quantity to do harm.

Marsh gas is formed by the action of a high temperature on many volatile and fixed organic bodies, and is an important constituent of coal gas; but the most convenient way to prepare it for use is to mix potassic acetate with two or three times its weight of slaked lime, and to heat the mixture in a flask coated with Stourbridge clay. Marsh gas is given off below a red heat, and carbonic acid remains in combination with the bases, partly potash, partly lime.

$$C^2H^3KO^2 + HKO^2 = CH^4 + CO^3K^2$$

represents the process, assuming potassic hydrate to react on the acetate. Marsh gas burns with a yellowish blue flame, but if previously heated by passing through a red-hot tube it is said to yield a far more luminous flame. One molecule of the gas, occupying two volumes, requires four atoms of oxygen, occupying four volumes, for its complete combustion, and the mixture explodes even more strongly than oxy-hydrogen gas. The products are two volumes of carbonic acid, four volumes of steam, of which latter the greater part condenses at the ordinary temperature and pressure. Marsh gas is the lightest known substance, next to hydrogen—its density being only 8. All attempts to condense marsh gas, by combined cold and pressure, have failed. Marsh gas is rather more soluble than oxygen in water, for at 0°C one volume of water dissolves 0.054; at 10°C 0.044; and at 20°C 0.035.

A succession of electric sparks decomposes marsh gas, carbon being deposited, and hydrogen being left, of volume double the marsh gas employed.

**74. Ethylene or Olefiant Gas** ($C^2H^4$) is one of the minor constituents of coal gas. It is best made by heating spirits of wine with about double its bulk of strong sulphuric

acid. Some dry sand should be added, in sufficient quantity to form a thick mud with the mixture, as is it otherwise liable to froth very much. The gas comes over with water, which is formed at the same time, by decomposition of the alcohol—

$$\text{Alcohol, } C^2H^6O = C^2H^4 + H^2O.$$

Some alcohol vapour is also carried over, as well as ether, and these impurities are best removed by passing the gas through oil of vitriol spread over pumice-stone. There is also sulphurous acid and carbonic acid formed, by the combustion of some of the alcohol at the expense of the sulphuric acid, and to remove these impurities the gas should be passed through caustic potash. It is then obtained as a colourless and nearly inodorous gas, of the same density as nitrogen and carbonic oxide, viz. 14.

Olefiant gas dissolves considerably in water. One volume at 0°C dissolves 0.256 of the gas, at 10° 0.184, and at 20° 0.149.

Faraday compressed olefiant gas to a liquid, by using a very great cold, together with pressure. At —76° the liquid was found to exert a pressure of 4.6 atmospheres, and at —17.8° as much as 26.9 atmospheres.

Olefiant gas burns with a bright luminous flame, consuming in the process three times its own volume of oxygen, and forming twice its own volume of carbonic acid. It is easily decomposed by heat, and if passed through a red-hot tube, it deposits carbon and forms marsh gas, together with other compounds; but at very high temperatures the marsh gas is in its turn decomposed, liberating hydrogen.

Olefiant gas is rapidly absorbed by anhydrous sulphuric acid, or by the fuming sulphuric acid (hydric disulphate), which is a compound of the acid with the hydric sulphate, and this re-agent is usually employed for absorbing olefiant gas in any mixture, such as coal gas, in which its quantity has to be determined. It is also absorbed, though very slowly, by common oil of vitriol (hydric sulphate), and the compound

thus formed is an acid salt of ethyle ($C^2H^5$) and hydrogen. By mixing this acid salt with water, and boiling the mixture, alcohol is distilled over, thus—

$$(C^2H^5)HSO^4 + H^2O = SO^4H^2 + C^2H^6O.$$

Through the agency of sulphuric acid, alcohol can therefore be built up again from olefiant gas and water, the very products into which it is decomposed, at a high temperature, by the acid itself.

Olefiant gas has obtained its name from the circumstance of its forming with chlorine an oily compound called Dutch liquid ($C^2H^4Cl^2$).

**75. Acetylene** ($C^2H^2$) is said to be formed by passing the vapour of Dutch liquid through a red-hot tube. It burns with a rather smoky flame. Its most characteristic property is that of forming a solid compound of a red brown colour when led into a solution of cuprous chloride in ammonia. This compound is explosive. By the action of hydrochloric acid the compound is decomposed with liberation of acetylene.

When warmed in contact with zinc, in a solution of ammonia, it gradually combines with the hydrogen which is being given off, and forms olefiant gas.

**76. Coal Gas** is a mixture of gaseous compounds given off by coals when rapidly heated to redness in an iron or earthenware retort. The quality of coal used for preparing gas is by no means a matter of indifference. The resinous coals yield far more gas than those harder varieties which do not cake on heating. Anthracite is of all kinds the most useless for gas making, as it approaches most nearly to coke in its composition. Cannel coal, and especially a substance known by the name of Boghead Cannel, are the best gas coals, and a ton of these yields as much as 15,000 cubic feet of gas. Ordinary varieties of blazing coal yield from 8,000 to 11,000 cubic feet per ton.

77. The gas deposits a good deal of semi-fluid matter

known by the name of tar, also water containing ammonia. Coal tar is alkaline to test-paper, and hydrochloric acid dissolves out from it a mixture of bases, containing carbon, hydrogen, and nitrogen, bases which can be precipitated from the hydrochloric acid by potash, and which appear as heavy oils. One of these is aniline ($C^6 H^7 N$), which is now largely manufactured for the preparation of dyes.

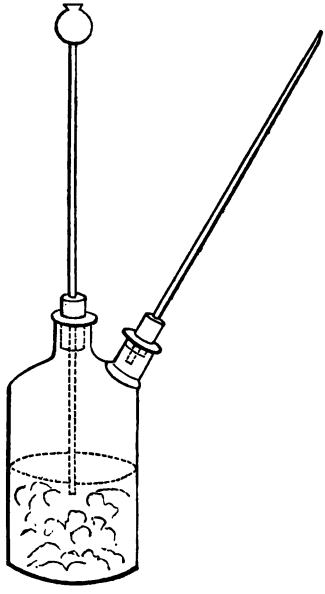
Coal tar also contains oily acids, which can be dissolved out from it by lime, and which are precipitated by hydrochloric acid. These are used for preserving meat and timber and other organic bodies from putrefaction and decay, and are generally called coal tar creosote. One chief antiseptic constituent of creosote is a crystalline body of the composition $C^6 H^6 O$, a kind of alcohol called phenilic hydrate.

Besides these basic and acid oils, coal tar contains several neutral oils and crystalline compounds. Among these benzole ($C^6 H^6$) and naphthaline ($C^{10} H^8$) deserve special mention. The former is the material from which aniline is artificially prepared, and the latter is a volatile solid which contributes materially to the peculiar smell of coal gas.

**78.** After it has deposited the tar, coal gas has to be purified before use. The worst impurity which it contains is sulphur, and this element is present partly in the form of sulphuretted hydrogen ($S H^2$), partly in the form of carbonic sulphide ($C S^2$). The sulphuretted hydrogen is removed by passing the gas over ferric hydrate, ferric sulphide and water being formed. The carbonic sulphide is left in the gas for want of a convenient method of removing it.

Ammonia should also be removed as completely as possible from the gas, not only for the sake of its commercial value for agricultural and other purposes, but also because it corrodes the brass tubes through which gas is passed. Sawdust soaked with dilute sulphuric acid is used for absorbing ammonia.

**79.** The greater proportion of the volume of coal gas consists of hydrogen and marsh gas, the former of which evolves heat and scarcely any light on combustion, while the latter is of very small illuminating value. In spite of this, hydrogen itself contributes to the illuminating value of coal gas, by keeping in it the vapour of benzole and of other highly illuminating liquids. A very simple experiment may prove this, for if a jet of hydrogen, which is burning at a fine point, be supplied with benzole, by pouring a few drops of the oil into the bottle in which the gas is being evolved, the flame immediately becomes white, or sometimes even smoky. Hydrogen and marsh gas are therefore of value by enriching the coal gas by benzole, or when present in the gas from Boghead Cannel they aid the evaporation of hydrocarbons, such as $C^5 H^{12}$. Carbonic oxide is a minor constituent of coal gas, which has a similar value. The actual illuminating gas contained in coal gas is olefiant gas, of which there is generally three to four per cent. of the volume of the mixture. In some varieties of gas there is besides olefiant gas a more easily condensible hydrocarbon, containing carbon and hydrogen in the same proportion as



Apparatus to shew flame of hydrogen charged with benzole.

olefiant gas, but differing from that body by its density, which is twice as great—viz. 28. This can be seen from its formula—$C^4H^8 = 2$ vols. This gas is often named after its illustrious discoverer, Faraday's gas. It is sometimes called butylene.

Carbonic acid and nitrogen are generally present in gas, in very small quantities. As an example of a coal gas, the following result of an analysis of a Manchester coal gas by Bunsen may be quoted. The numbers represent volumes of each constituent in 100 volumes of the gas.

| | | | |
|---|---|---|---|
| Hydrogen . . . . | 45.58 | Butylene . . . . | 2.38 |
| Marsh gas . . . . | 34.90 | Sulphuretted hydrogen | 0.29 |
| Carbonic oxide . . | 6.64 | Nitrogen . . . . | 2.46 |
| Olefiant gas . . . | 4.08 | Carbonic acid . . . | 3.67 |

Acetylene is also frequently contained in coal gas.

**80.** The flame of a common candle or oil lamp differs from a flame of gas mainly in one respect; namely, that it is a gas manufactory as well as a gas burner. For the liquid fat or oil is drawn up by the wick, in the midst of the flame, where it is made into gas by the action of heat, and the gas burns all round the wick as fast as it is formed, evolving (by its combustion) heat, which keeps up the supply of gas. Immediately round the wick of a candle the flame does not give light, and this dark zone extends usually to some height above the wick. It consists of combustible gases, on their way from the wick to the outer part of the flame, where they get burnt.

Immediately round this inner and non-luminous zone is the brighter part of every flame. It consists mainly of steam, formed by the combustion of hydrogen, and solid particles of carbon, heated to a bright white heat. Of course nitrogen penetrates into it, with the oxygen which goes to form steam. A clear bead of glass held in this part of the flame by a platinum wire or forceps, gets blackened by collecting soot,

and metallic oxides—such as plumbic oxide—which part with their oxygen easily are reduced to the metallic state. This flame, containing free carbon, is therefore called the reducing flame.

The outer surface and the top of the flame is usually of a pale blue or violet colour, and consists of carbonic acid and steam, mixed with nitrogen and heated to a high temperature by the complete combustion of the gas. This outer flame is called the oxidizing flame, as it produces powerful effects of oxidation, owing to the presence in it of atmospheric air, at a high temperature.

Whenever hydrocarbons are very imperfectly burnt, there is a deposition of carbon, as the more active hydrogen gets oxidized first; and this temporary deposition of carbon is an essential condition for the production of the white light required in an ordinary flame.

When coal gas is wanted for heating purposes it can be burnt in Bunsen burners, which are so constructed that the coal gas mixes in a tube with a certain limited quantity of air, and the mixture burns in the open air on coming out of this tube. Under these circumstances a pale violet colour is alone visible in the flame, and it is scarcely more luminous than a similar flame of hydrogen. When a more intense heat is needed, the flame is supplied by a jet of air from the nozzle of a mouth blow-pipe, or, better still, a blow-pipe worked by bellows; and in this manner glass tubes or rods can be readily heated so as to bend to any required angle, or even to draw out to a fine point.

## APPENDIX TO CHAPTER XI.

### PROBLEMS.

79. What is the weight of 10 litres of marsh gas at 0°C and 760 mm.?

80. What volume of air is needed for the complete combustion of a litre of marsh gas? What will be the volume (calculated at 0°C and 760 mm.) of the steam formed by its combustion?

81. What weight of marsh gas would be obtained from a kilogramme of potassic acetate, according to the equation

$$KC^2H^3O^2 + KHO = CH^4 + K^2CO^3?$$

82. What is the volume of a kilogramme of ethylene?

83. What volume of oxygen is needed for the complete combustion of a litre of olefiant gas? What volume of carbonic acid, and what volume of steam, are formed?

84. What volume of hydrogen would be obtained from a litre of olefiant gas if the carbon were entirely removed?

85. What volume of acetylene could be burned by a litre of oxygen? What would be the volumes of the products?

86. What is the weight of a litre of acetylene?

87. A thousand litres of olefiant gas are burned in a chamber containing 100 cubic meters of dry and pure air, both at 0°C and 760 mm. What is the percentage composition of the air at the end of the process, supposing nothing to escape?

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# CHAPTER XII.

**81. Cyanogen** ($C^2N^2$) is best prepared by heating mercuric cyanide in a glass tube. It should be collected over mercury, or by displacement of air, as water dissolves it to a considerable extent. Metallic mercury is set free, together with cyanogen gas; but some of the cyanogen is transformed into a dark brown mass containing carbon and nitrogen.

Cyanogen is a heavy gas of pungent odour. Its density is 26. It burns with a purple flame, absorbing twice its bulk of oxygen. When passed through a tube cooled to a temperature of — 25° to — 30°C it condenses to a liquid, and at 0°C the liquid was found by Bunsen to exert a pressure of 2.7 atmospheres; at 20°C of 5 atmospheres. The liquid freezes at — 34.4°. When dissolved in water cyanogen speedily decomposes, forming a variety of products; amongst them is ammonia oxalate, formed by cyanogen taking up the elements of water—

$$C^2N^2 + (H^2O)^4 = C^2(NH^4)^2O^4.$$

Cyanogen combines with potassium, but the compound (K C N) is easily decomposed by acids, in presence of water. Cyanogen is remarkable for the stability of the double salt, which it forms with iron and potassium, and for the instability of its compounds with the alcali metals by themselves. With iron it forms the valuable blue colours known by the name of Prussian blue.

**82. Cyanic Acid** is assumed to exist in the so-called cyanates, represented by hydric cyanate (H C N O). It is prepared by distilling hydric cyanurate or cyamelide; the condenser should be surrounded by a freezing mixture. It is a very volatile liquid, of pungent odour and violent action on the skin. Even at the temperature of 0°C this compound speedily changes into a solid inert substance, called cyamelide; but at the ordinary atmospheric temperature the change is complete in five minutes. When dissolved in water, cyanic acid is recognised for a short time by its peculiar odour, but it soon takes up the elements of water, and becomes converted into hydro-ammonic carbonate—

$$CNOH + (H^2O)^2 = CO^3HNH^4.$$

**83. Urea** ($CON^2H^4$) is a weak base contained in human urine, and constituting the chief nitrogenized excretion. It can be obtained by adding nitric acid to urine, previously

evaporated to a small bulk. Impure crystals of urea nitrate are thus deposited, and urea can be obtained from them by evaporating their solution in water to dryness with barytic carbonate in slight excess, and dissolving up the urea by alcohol, which leaves barytic nitrate undissolved.

Urea contains the elements of ammonia cyanate—

$$NH^4(CNO);$$

and this suggested to Wöhler the possibility of making it artificially by combining ammonia and hydric cyanate. The usual plan is to mix a solution of potassic cyanate in water with ammonia sulphate, and to evaporate the mixture to dryness. The quantity of sulphate should be sufficient to supply fully as much sulphuric acid as the potassium in the cyanate requires. Alcohol is added to the dry mixture, and dissolves out urea from it, leaving potassic sulphate and the excess of ammonia salt. The process consists of an interchange of bases, between the potassic cyanate and ammonia sulphate, forming ammonia cyanate and potassic sulphate—

$$(KCNO)^2+(NH^4)^2SO^4=K^2SO^4+(NH^4CNO)^2;$$

and part of the ammonia salt is changed into urea, while another part takes up water, becoming neutral ammonia carbonate. By evaporation of its solution urea is obtained in the form of white needle-shaped crystals, which dissolve readily in water.

The urea nitrate is considerably less soluble in water than the base itself. Its composition is represented by the formula $(NO^3H)CN^2H^4O$. Nitrous acid immediately decomposes urea with effervescence; carbonic acid and nitrogen being given off whilst water is formed. When mercuric nitrate is added to a solution of urea, a white precipitate is formed, containing urea combined with mercuric oxide and a part of the nitric acid.

Urea oxalate is precipitated when a concentrated aqueous solution of urea is mixed with oxalic acid. Its formula is

$(C N^2H^4O)^2 H^2C^2O^4$. In contact with decomposing animal or vegetable matter urea combines with the elements of water, and is transformed into ammonia carbonate. Hence the presence of that salt in decomposed urine—

$$C O N^2H^4 + (O H^2)^2 = C O^3 (N H^4)^2.$$

Urea is decomposed by heat. It first melts, and then gives off ammonia. When as much ammonia as possible has been expelled by heat, the residue possesses the composition of cyanic acid or cyamelide, but different properties from either of these bodies. It is called 'cyanuric acid.'

**84. Cyanurates.**—The hydrogen salt $H^3C^3N^3O^3$ is a solid crystallizable compound of great stability. It is purified by dissolving in oil of vitriol with the aid of heat, and adding nitric acid as long as there is any effervescence. Water then precipitates a snowy-white powder, which is pure cyanurate. A solution of cyanurate in water does not decompose like the corresponding solution of a cyanate.

The basic metal in cyanurates is replaceable in three proportions, forming double salts of the three following classes; viz., 1st, those in which one atom of hydrogen is replaced by the more basic metal, for instance $K H^2C^3N^3O^3$; 2nd, salts which are formed by the substitution of metal for two atoms of hydrogen, such as $H Ag^2C^3N^3O^3$; and, finally, salts in which all the three atoms of hydrogen are replaced by basic metal, such as $Ag^3C^3N^3O^3$. This shews that the molecule of the hydrogen salt contains three atoms of hydrogen.

Hydric cyanate has only one atom of hydrogen in each molecule, for we cannot remove a part of the hydrogen in one molecule without removing the whole.

Hydric cyanurate passes over into the cyanate by mere distillation, without taking up or losing anything; and cyamelide can be transformed in like manner into hydric cyanate without any change in the proportions of the elements contained in it.

**85.** The term '**isomerism**' is used to denote the existence of differences of physical or chemical properties among bodies of the same composition. A fourth substance of considerable importance (besides cyanilic acid) is isomeric with these three, viz. fulminic acid. This body is only known in its salts, the fulminates, of which the commonest is the mercury salt, a detonating compound used for charging percussion caps.

The salt is made by the action of nitrous acid on alcohol, in presence of a salt of mercury, and the violence with which it detonates when struck or heated finds no parallel in the case of any other of the isomeric bodies. Argentic fulminate is represented by the formula $Ag^2C^2N^2O^2$; and there is a double salt containing silver and potassium according to the proportions $AgKC^2N^2O^2$, which leaves no doubt that the hydrogen salt itself, if prepared, would be found to possess the composition $H^2C^2N^2O^2$.

We have therefore the series of salts—

| | |
|---|---|
| Cyanate . . . . . | HCNO, |
| Fulminate . . . . | $H^2C^2N^2O^2$, |
| Cyanurate . . . . | $H^3C^3N^3O^3$. |

**86. Cyanides.**—Hydric cyanide, commonly called prussic acid, is most conveniently prepared by adding dry calcic chloride gradually to the aqueous solution of the acid until considerably more is added than the liquid can dissolve, and then distilling the mixture at a very gentle heat, using as a condenser a vessel surrounded by a freezing mixture. In the dry state, as thus obtained, prussic acid is so exceedingly dangerous a substance, that it ought never to be made without a very good reason, and extreme care. It is a light mobile liquid, which boils at about 27°C, and evaporates in large quantities far below its boiling-point. A small quantity of the vapour is sufficient to produce instantaneous death.

It burns rapidly in the air, absorbing $1\frac{1}{4}$ times its volume of oxygen in the process.

It dissolves in water in all proportions, but is held with very little force, so that even when diluted with much water the acid evaporates very easily.

To prepare a solution of prussic acid the usual plan is to decompose a solution of potassic ferro-cyanide by dilute sulphuric acid, and distil with a good condenser, and some cold water in the receiver. The best proportions are: 10 grammes of the crystallized ferro-cyanide dissolved in 50 grammes of water; 3.5 grammes of common sulphuric acid are then mixed with 25 grammes of water, and the mixture when cold is poured into the solution of the salt. On distilling this mixture a greenish white precipitate is formed, containing half the cyanogen of the salt employed, in combination with all the iron and one-quarter of the potassium.

The reaction is thus stated by equation—

$$2\,(Fe\,K^4\,(CN)^6) + 3\,(H^2SO^4) + Aq = Fe^2K^2(CN)^6 + \\ + 3\,(K^2SO^4) + 6\,(HCN) + Aq.$$

The solution of prussic acid has a strong smell of the acid. It reddens litmus-paper very slightly indeed; has so little tendency to take potassium in place of its hydrogen that it is not even able to decompose a solution of potassic carbonate. When mixed with a solution of potash, prussic acid is decomposed, forming potassic cyanide and water—

$$CNH + HKO = CNK + H^2O;$$

but the solution is as alkaline to test paper as caustic potash itself. It is decomposed by carbonic acid of the air or breath:

thus $CNK + CO^3H^2 = CNH + CO^3HK$;

hence the smell of prussic acid which it possesses.

A solution of prussic acid is liable to undergo decomposition, especially when exposed to the sunshine. A small quantity of hydrochloric acid impedes the decomposition, and is therefore usually added to prussic acid in order to

preserve it; but concentrated hydrochloric acid decomposes the cyanide immediately, forming ammonia and formic acid: thus,

$$CNH + (H^2O)^2 + HCl = NH^3HCl + CH^2O^2.$$

When prussic acid is boiled with an excess of potash, ammonia is evolved, and formic acid remains in combination with the potash. Strong sulphuric acid not only acts like hydrochloric acid, in decomposing prussic acid, but when heated with the products causes a secondary decomposition of the formic acid into carbonic oxide and water. The action of heat upon ammonia formiate gives rise to prussic acid and water ($CNH^4HO^2 - (H^2O)^2 = CNH$).

Prussic acid is recognized by a variety of tests, which are characteristic and delicate. When added to argentic nitrate it forms a precipitate consisting of argentic cyanide, and this precipitate dissolves in ammonia or in boiling nitric acid.

With solution of mercurous nitrate it forms a grey precipitate consisting of metallic mercury, whilst mercuric cyanide remains in the solution.

When neutralized by potash and heated with a solution of ferrous sulphate it forms potassic ferro-cyanide, which can be separated by filtration from ferric oxides and discovered by acidulation with hydrochloric acid, and addition of ferric-chloride, which precipitates Prussian blue.

By evaporation to dryness with yellow ammonia sulphide, prussic acid combines with sulphur, and the residue, dissolved in water, gives a deep blood-red colour when mixed with ferric chloride—

$$(NH^4CNS)^6 + Fe^2Cl^6 = Fe^2(CNS)^6 + (NH^4Cl)^6.$$

**87. Methylamine** ($CNH^5$). In the presence of spongy platinum prussic acid vapour combines with hydrogen, forming a compound wonderfully like ammonia in its properties, and called methylamine. This remarkable base will be more fully described hereafter. Its vapour has the same power of

saturating acids as an equal volume of ammonia, and $CNH^5$ may be considered equivalent to $NH^3$. Methylamine can be condensed to a liquid at the atmospheric pressure, at a temperature but little below o°C. Its vapour burns easily, forming carbonic acid and water, and liberating nitrogen.

## APPENDIX TO CHAPTER XII.

### PROBLEMS.

88. What is the weight of a litre of cyanogen?

89. What volume of air is needed for the combustion of a litre of cyanogen? What volume of each product is formed?

90. What weight of ammonia could be obtained from one gramme of urea?

91. What weight of urea nitrate could be obtained by saturating one gramme of urea with nitric acid?

92. If a gramme of argentic fulminate were broken up into metallic silver, carbonic oxide, and nitrogen, what volume of each of the gases would you obtain?

93. What weight of hydrocyanic acid is obtained by distilling 500 grammes of crystallized "ferro-cyanide" $((CN)^6 Fe K^4 (H^2O)^3)$ with dilute sulphuric acid?

94. What is the volume of ten grammes of methylamine? What volume of oxygen is needed for their combustion? What volume of each product is formed?

# CHAPTER XIII.

**88. Atomic theory.** Each element consists of small indivisible particles called atoms. The elementary atoms are capable of uniting with one another, forming compounds, but they cannot be destroyed by any known process. Each atom of oxygen has the same weight as any other atom of oxygen, so also with hydrogen, nitrogen, carbon, &c.; in fact all the atoms of one element have the same weight; and chemistry teaches that an atom of oxygen is sixteen times as heavy as an atom of hydrogen, and this is meant when we say that 16 is the atomic weight of oxygen. An atom of nitrogen is fourteen times as heavy as an atom of hydrogen, so that the atomic weight of nitrogen is 14; and an atom of carbon is twelve times as heavy as an atom of hydrogen, so that the atomic weight of carbon is 12. In like manner the atomic weigh of each of the other elements tells us the weight of every atom of that element, taking the weight of the atom of hydrogen as *one.*

Each atom has different properties under different circumstances: its own weight is, however, a property which each atom retains under all circumstances. Thus the volume or tension of oxygen increases with rise of temperature, and the velocity with which its atoms diffuse through an opening in a vessel increases also. With some substances, such as mercury, oxygen does not combine at the ordinary temperature; but at a higher temperature the oxygen is converted by contact with mercury into a solid red powder which contains the atom of mercury united with the atom of oxygen in couples (HgO). The atoms of mercury are in as solid a state as those

of a solid bar of the metal frozen by carbonic acid; and the atoms of oxygen which no combination of cold and pressure has yet been sufficient to reduce even to the liquid state, are in the mercuric oxide perfectly solid.

**89. Molecule** is the name given to the smallest cluster of atoms of any compound that is believed capable of existing by itself, and every pure compound consists of similar molecules.

Every compound has a molecular weight equal to the sum of the atomic weights of the elementary atoms contained in it. Thus, formic acid ($C O^2 H^2$) has a molecular weight $12 + 2 \times 16 + 2 = 46$; and less than 46 parts by weight of formic acid can never be represented as taking part in any chemical reaction. Oxalic acid ($C^2 O^4 H^2$) might, consistently with the atomic weights of its elements, be represented by the formula $C O^2 H$, but the study of its derivatives has shewn that the molecule of the acid does contain two atoms of hydrogen; for we can take out one atom of hydrogen and put in one atom of potassium in its place, forming the hydropotassic oxalate $C^2 O^4 H K$; or we can replace both atoms of hydrogen by potassium in a similar manner, forming the neutral potassic oxalate $C^2 O^4 K^2$. The molecule of ammonia is represented by the formula $N H^3$; for one-third of the hydrogen can be taken out and replaced by an atom of another kind, or two-thirds of the hydrogen can be taken out and replaced, or, finally, the whole of the hydrogen can be replaced by three atoms of some other element.

The molecular weight of a hydrogen salt is that weight which contains as many atoms of hydrogen replaceable by potassium or silver as have been separately replaced by such a metal. Hydric oxalate and carbonate have the molecular formulæ $C^2 O^4 H^2$ and $C O^3 H^2$, because potassium can replace either one or both atoms of hydrogen in these formulæ. Nitrate and chlorate have the molecular formulæ

$NO^3H$ and $ClO^3H$, because potassium never replaces part of the hydrogen in one of the acids, so as to form a compound derivable from any multiple of these formulæ, having part of the hydrogen replaced by potassium. There is no hydropotassic nitrate or hydropotassic chlorate with such a formula as $N^2O^6HK$, or $N^3O^9H^2K$, or $N^3O^9HK^2$, &c.

**90.** The term 'atom' was explained above only in its application to elements. It is, however, applied to compounds, in accordance with the same principles which regulate its application to elements. Whenever a group of elements forms a compound corresponding to one formed by an element, or in fact, whenever a group behaves like an element, such group of elements is called a radical, and the term 'atom' is applied to radicals exactly in the same way as it is applied to elements. Thus $NH^4$ is a radical analagous to potassium, and $NH^4$ is capable in many compounds of taking the place of K. $NH^4$ is called an atom of ammonium.

In like manner CN combines in a similar manner to Cl, and is a radical comparable to the element chlorine. CN is called an atom of cyanogen. But neither $NH^4$ nor CN are believed capable of existing by themselves, any more than Cl. If ammonium be ever made, its molecule will doubtless be found to correspond to the formula $(NH^4)^2$, just as the molecule of cyanogen is found to be $(CN)^2$, and the molecule of chlorine is $Cl^2$.

**91.** The elements oxygen, nitrogen, and carbon, form with hydrogen the compounds $H^2O$, $H^3N$, $H^4C$. Each atom of oxygen is here combined with two atoms of hydrogen, each atom of nitrogen is combined with three atoms of hydrogen, and each atom of carbon is combined with four atoms of hydrogen; and these quantities of the three compounds occupy precisely the same volume in the state of vapour, so that a cubic centimeter of ammonia gas has got

three atoms of hydrogen in it, for every two atoms of hydrogen in a cubic centimeter of steam; and a cubic centimeter of marsh gas has got four atoms of hydrogen in it for every two atoms of hydrogen in an equal volume of steam, or for every three atoms of hydrogen in the cubic centimeter of ammonia. In each molecule of olefiant gas, $(C^2 H^4) = (C H^2)^2$, there are only two atoms of hydrogen to each atom of carbon.

There are other elements, such as chlorine, potassium, silver, &c., which resemble hydrogen in the atomic constitution of their compounds with oxygen, nitrogen, and carbon. They form, for instance, the compounds $Cl^2 O$, $K^2 O$, $Ag^2 O$, $Cl^3 N$, $K^3 N$, $Ag^3 N$, $Cl^4 C$, &c., so that one atom of oxygen combines with two atoms of hydrogen, or of these other elements. Nitrogen combines with three atoms of hydrogen, or three of these other elements; and so also the atom of carbon combines with four atoms of elements of the hydrogen class.

The term 'biatomic' is used to denote this power which the atom of oxygen possesses of combining with two atoms of the hydrogen class. Nitrogen is similarly called triatomic; and carbon is tetratomic in marsh gas, and apparently biatomic in olefiant gas. In acetylene it would appear to be monatomic, but we shall see evidence that such is not really the case.

When hydrogen combines with chlorine, or any other element of its own class, it is always in the proportion of one atom of each; so that hydrogen is a monatomic element.

Many of the most important peculiarities of compounds depend upon the atomicity of the elements contained in them.

When marsh gas is burnt, the formula

$$C H^4 + O^4 = C O^2 + H^4 O^2$$

describes the atomic proportions in which the process takes place. The product $C O^2$ has been formed from $C H^4$ by

taking away the four atoms of hydrogen and putting in two atoms of oxygen in their place. And in like manner the other product, $H^4O^2$, is formed by taking out one atom of carbon from each molecule of marsh gas, and replacing it by two atoms of oxygen. In describing this result it is customary to say that two atoms of oxygen are 'equivalent to' four atoms of hydrogen, and that two atoms of oxygen are 'equivalent to' one atom of carbon. The term 'equivalent' is really synonymous with 'capable of replacing.' It is not intended to convey the idea of any equality of properties.

When prussic acid is burnt, the equation

$$(CNH)^2 + O^5 = (CO^2)^2 + N^2 + H^2O$$

represents the atomic proportions of the process; and the carbonic acid is formed by four biatomic atoms of oxygen taking the place of two triatomic atoms of nitrogen, and of two monatomic atoms of hydrogen. The sum of the atomicities of the oxygen going into combination, is equal to the sum of the atomicities of the elements going out of the compound. This relation holds good in all decompositions in which the elements retain their original atomicities.

**92.** When olefiant gas is completely burnt the reaction is $C^2H^4 + O^6 = (CO^2)^2 + (H^2O)^2$. The four monatomic atoms of hydrogen in the olefiant gas are here replaced by four biatomic atoms of oxygen, and the apparent atomicity of the carbon is doubled.

If four atoms of oxygen only were supplied to each molecule of olefiant gas, and half of it combined with the hydrogen, while the other half combined with the carbon, forming carbonic oxide,—$C^2H^4 + O^4 = (CO)^2 + (H^2O)^2$,—the four monatomic atoms of hydrogen would be replaced by two biatomic atoms of oxygen, and the carbon would continue apparently biatomic.

## *Elements of Uneven Atomicity.*

| Monads. | | | | Triads. | | | |
|---|---|---|---|---|---|---|---|
| Hydrogen | H | = | 1 | Nitrogen | N | = | 14 |
| Fluorine | F | = | 19 | Phosphorus | P | = | 31 |
| Chlorine | Cl | = | 35.5 | Arsenic | As | = | 75 |
| Bromine | Br | = | 80 | Antimony | Sb | = | 122 |
| Iodine | I | = | 127 | Bismuth | B | = | 210 |
| Lithium | Li | = | 7 | Boron | B | = | 11 |
| Sodium | Na | = | 23 | Gold | Au | = | 196 |
| Potassium | K | = | 39 | | | | |
| Rubidium | Rb | = | 85 | | | | |
| Cœsium | Cs | = | 133 | | | | |
| Thallium | Tl | = | 203 | | | | |
| Silver | Ag | = | 108 | | | | |

## *Elements of Even Atomicity.*

Dyads, Tetrads, &c.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Oxygen | O | = | 16 | Cerium | Ce | = | 92 |
| Sulphur | S | = | 32 | Lanthamum | La | = | 92 |
| Selenium | Se | = | 79.5 | Didimium | Di | = | 96 |
| Tellurium | Te | = | 129 | Uranium | U | = | 120 |
| Calcium | Ca | = | 40 | Zirconium | Zr | = | 89.5 |
| Strontium | Sr | = | 87.5 | Tantalum | Ta | = | 138 |
| Barium | Ba | = | 137 | Niobium | Nb | = | 195 |
| Lead | Pb | = | 207 | Thorinum | Th | = | 238 |
| Mercury | Hg | = | 200 | Carbon | C | = | 12 |
| Magnesium | Mg | = | 24 | Silicon | Si | = | 28 |
| Zinc | Zn | = | 65 | Tin | Sn | = | 118 |
| Cadmium | Cd | = | 112 | Titanium | Ti | = | 50 |
| Indium | In | = | 74 | Molybdenum | Mo | = | 96 |
| Aluminium | Al | = | 27.5 | Vanadium | V | = | 137 |
| Iron | Fe | = | 56 | Tungsten | W | = | 184 |
| Chromium | Cr | = | 52.5 | Platinum | Pt | = | 197 |
| Manganese | Mn | = | 55 | Iridium | Ir | = | 197 |
| Cobalt | Co | = | 58.5 | Osmium | Os | = | 199 |
| Nickel | Ni | = | 58.5 | Rhodium | Ro | = | 104 |
| Copper | Cu | = | 63.5 | Ruthenium | Ru | = | 104 |
| Glucinum | G | = | 9 | Palladium | Pd | = | 106.5 |
| Yttrium | Y | = | 64 | | | | |

# CHAPTER XIV.

**93. Chlorine** (Cl 35.5 = 2 vols.) is most conveniently prepared by heating finely-powdered manganic peroxide with strong hydrochloric acid. The manganese seems at first to dissolve as perchloride ($Mn Cl^4$), but chlorine gas speedily comes off, leaving manganous chloride—

$$Mn O^2 + (H Cl)^4 = Mn Cl^2 + Cl^2 + (H^2O)^2.$$

When the mixture is heated in a closed tube, similar to that described for the preparation of liquid ammonia, liquid chlorine is obtained. At 15.5° it requires a pressure of four atmospheres for its liquefaction. At the ordinary atmospheric pressure chlorine is a yellow gas, about two and a-half times as heavy as air. Its density is 35.5. At 15°C water dissolves about twice its volume of chlorine gas, and for this reason it is customary to collect the gas by displacement of air.

The gas has a most suffocating odour, and even two or three per cent. of it renders air quite irrespirable, as it disorganizes the tissues of the air-passages of the lungs. It forms a crystalline hydrate of the composition, $Cl (H^2O)^5$.

Chlorine combines with metals, and its compounds are called chlorides. Powdered metallic antimony showered into the gas catches fire. Finely-divided metallic iron also burns in chlorine. In the dry state chlorine does not affect the colour of litmus-paper, but a drop of water thrown on the paper causes the immediate destruction of the colour by chlorine. Some colouring matters are bleached by chlorine alone, but the greater number of bleaching effects produced by it are with the co-operation of water.

When passed with steam through a red-hot tube chlorine combines with hydrogen, and liberates oxygen from a portion of the steam.

When passed into a solution of ammonia it gives off nitrogen gas by taking hydrogen from the ammonia. But when passed into a solution of sal-ammonia chlorine forms oily drops of nitric chloride, which fall to the bottom of the liquid and detonate with great violence on very slight provocation.

A solution of caustic potash absorbs chlorine, the first product being potassic chloride and a salt of potash with hypochlorous acid—

$$Cl^2 + (H\,K\,O)^2 = Cl\,K + Cl\,K\,O + H^2O.$$

**94.** Chlorine forms four acid compounds with hydrogen and oxygen, and salts corresponding to them. They are called perchlorates (such as $Cl\,O^4\,H$), chlorates (such as $Cl\,O^3\,H$), chlorites (such as $Cl\,O^2\,H$), and hypochlorites (such as $Cl\,O\,H$). Anhydrous acids corresponding to two of these are known, viz. chlorous acid ($Cl^2\,O^3$), and hypochlorous acid ($Cl^2\,O$). There is also a neutral peroxide, $Cl^2\,O^4 = 4$ vols. Hydric perchlorate ($H\,Cl\,O^4$) can be obtained by decomposing a solution of potassic perchlorate by hydrofluosilicic acid. The potassium is carried down as fluosilicate, while hydric perchlorate is formed—

$$Si\,Fl^6\,H^2 + (Cl\,O^4\,K)^2 = Si\,Fl^6\,K^2 + (Cl\,O^4\,H)^2.$$

When obtained as a monohydrate, perchloric acid is a liquid of 1.78 density at 15.5° (Roscoe). In contact with charcoal it explodes with great violence. The acid forms a crystalline terhydrate, $Cl\,O^4\,H\,H^2O$. Dilute solutions of perchloric acid dissolve zinc with evolution of hydrogen, and formation of zinc perchlorate. Chloric acid (hydric chlorate) is best prepared by adding dilute sulphuric acid to a solution of barytic chlorate, in quantity exactly sufficient to combine with all the barium, without leaving any sulphuric acid mixed

*with* the chloric acid. Barytic sulphate is completely precipitated—

$$Ba(ClO^3)^2 + SO^4H^2 = (ClO^3H)^2 + SO^4Ba.$$

The solution of chloric acid may be concentrated, by evaporation at a gentle heat; but the process should be completed by putting the partially concentrated acid into a vacuum beside some strong sulphuric acid. Chloric acid, when containing but a little free water, is decomposed by light, and becomes yellow, owing to the formation of chlorous acid. It is decomposed by distillation, perchloric acid being formed, besides other products. A piece of blue litmus-paper is reddened by strong chloric acid, but a bleaching action immediately follows. Chloric acid is a powerful oxidizing agent, and presents many points of analogy with nitric acid. It is monobasic, and is remarkable for the solubility of its salts. Even the argentic, plumbic, and barytic chlorates are soluble in water.

Strong sulphuric acid decomposes chloric acid, with evolution of a deep yellow gas, which explodes when gently heated. Oxygen is given off at the same time, and the yellow gas called chloric peroxide appears to have the composition $Cl^2O^4 = 4$ vols.

Chlorous acid is obtained by the partial desoxidation of chloric acid. It is a weaker acid than chloric acid, but presents in other respects great resemblance to it.

**Hypochlorous Acid** (Cl O H) is obtained by shaking up chlorine water with mercuric oxide. Its solution in water is colourless, and has a peculiar sickly odour. It is an exceedingly weak acid, being expelled by carbonic acid from its salts in presence of water. In the free state it is an exceedingly powerful bleaching agent, and is present together with hydrochloric acid in the solution of chlorine in water. There is no difficulty in removing the hydrochloric acid from the solution, by adding to it a solution of argentic nitrate

as long as any precipitate is formed. The decomposition is thus represented—

$$Cl^2 + H^2O + NO^3Ag = ClAg + ClOH + NO^3H.$$

After the action of the nitrate has removed half the chlorine the solution retains all the bleaching power which it had before the silver salt was added. When concentrated, hypochlorous acid is mixed with concentrated hydrochloric acid, an action takes place in the reverse direction to that of chlorine on water—

$$ClH + ClOH = Cl^2 + H^2O.$$

Anhydrous hypochlorous acid ($Cl^2O = 2$ vols.) is obtained in the form of a yellow gas by passing chlorine over red oxide of mercury, both substances being dry.

The compound so much used by the name of bleaching powder is a mixture of calcic hypochlorite with calcic chloride. Hypochlorous acid can be liberated by adding dilute sulphuric acid, little by little, to bleaching powder mixed with water, and agitating the mass whilst the acid is running into it. In this manner the weak hypochlorous acid is alone set free, and can be distilled over. If too much sulphuric acid were to be added, hydrochloric acid would also be evolved from the calcic chloride, and would evolve chlorine, with the hypochlorous acid in the liquid.

**95. Hydrochloric Acid** ($HCl = 2$ vols.), frequently called muriatic acid, is formed when a mixture of equal volumes of chlorine and hydrogen is exposed to the sunshine; the mixture explodes, forming hydrochloric acid gas of the same volume as the mixture. The elements are not known to combine in any other proportion. On a small scale the gas is most conveniently made by heating strong sulphuric acid with lumps of table salt, of the size of hazel nuts, obtained by melting the salt in an earthen crucible, and pouring it out to cool on a stone, then breaking up the cake into fragments of the size described. Half of the hydrogen of the sulphate is replaced

*by* the sodium of the salt, forming hydrosodic sulphate, and the hydrogen which leaves the sulphate goes away in combination with chlorine from the salt. Thus,

$$S O^4 H^2 + Na Cl = S O^4 H Na + H Cl.$$

For manufacturing purposes a similar operation is performed with only half the proportion of sulphuric acid, aided by much stronger heat. The first part of the process then takes place as above, but the hydrosodic sulphate subsequently reacts on a molecule of salt, forming neutral sodic sulphate and hydrochloric acid—

$$S O^4 H Na + Na Cl = S O^4 Na^2 + H Cl.$$

The density of the gas is 18.75. At 10°C a pressure of 40 atmospheres is required to liquefy hydrochloric acid. Hydrochloric acid forms dense fumes when allowed to escape into moist air. It dissolves in water with great avidity, giving off considerable heat, and forming a solution of greater density than water. When containing about 40 per cent. of acid, the solution has a density of 1.2. Strong solutions give off hydrochloric acid gas when heated, and they boil constantly at 110°C. Weak solutions give off water, with but little hydrochloric acid, until their boiling-point has risen to 110°C at the ordinary atmospheric pressure. At this temperature the solution distils uniformly, and contains about 20 per cent. of hydrochloric acid. Roscoe finds that if the solution is distilled under a pressure of two atmospheres, it distils over undecomposed when containing 19 per cent. of acid; and at a pressure of three atmospheres it distills regularly only when containing about 18.3 per cent. H Cl.

**96.** Hydrochloric acid is an exceedingly acid salt, and by double decomposition with potassic hydrate it forms potassic chloride and water, both neutral bodies. There is only one proportion in which the hydrogen of hydrochloric acid can be removed, in whatever proportions the acid salt

may be mixed with the basic compound. The process is this: $H Cl + H K O = K Cl + H^2 O$.

In any solution hydrochloric acid can be detected by the characteristic curdy precipitate which it forms with argentic nitrate. The precipitate, which consists of argentic chloride, is insoluble in nitric acid, even on boiling, but dissolves readily in ammonia. Mercurous nitrate is also decomposed by dilute hydrochloric acid, forming a precipitate of mercurous chloride, generally known by the name of calomel—

$$(N O^3)^2 Hg^2 + H^2 Cl^2 = (N O^3 H)^2 + (Cl Hg)^2.$$

One of the most characteristic properties of hydrochloric acid is that of yielding a volatile compound with chromium and oxygen, called chlorochromic acid. The compound is easily obtained by evaporating hydrochloric acid to dryness with potash, and mixing the dry potassic chloride with potassic dichromate and plenty of strong sulphuric acid, and distilling the mixture in a retort, when a deep-red vapour having the composition $Cr O^2 Cl^2$ goes over into the receiver.

Strong hydrochloric acid is oxidized by strong nitric acid, chlorine and oxides of nitrogen being evolved. The mixture is called aqua regia, from its property of dissolving gold or platinum, metals which are not attacked by either nitric or hydrochloric acid alone.

Commercial hydrochloric acid is very liable to contain arsenic, and not unfrequently sulphurous acid.

**97. Nitric Chloride** ($N Cl^3$) is obtained by passing chlorine into a solution of sal-ammonia. It gradually goes to the bottom of the liquid, and is most safely collected in a hollow block of lead. A great number of organic bodies possess the property of causing this compound to explode, and the violence with which it explodes is so great as to shatter any glass or earthenware vessel.

The products of the decomposition are free nitrogen and chlorine.

**Chloronitric Acid** ($NO^2Cl$) is obtained by the action of chlorophosphoric acid on plumbic nitrate. It is a heavy liquid, which is decomposed by contact with water, forming hydrochloric and nitric acids—

$$NO^2Cl + H^2O = HCl + NO^3H.$$

**Chloronitrous Acid** ($NOCl$ = 2 vols.) is one of the substances formed by the action of nitric acid on hydrochloric acid. It can be condensed by a frigorific mixture from the vapours given off by aqua regia. Nitric oxide combines directly with chlorine, forming this compound.

**98. Ammonia Chloride** ($NH^4Cl$ = 4 vols.). This salt is commonly called sal-ammonia, and sometimes muriate of ammonia.

It is usually made in this country by adding hydrochloric acid to the so-called gas liquor, which is an impure solution of ammonia, containing carbonic acid, sulphuretted hydrogen, and other weak acids. The crude salt is purified by crystallization, by heating the crystals, and finally by sublimation. It is very soluble in water, and by evaporation of its solution the salt can be obtained in cubical, or sometimes in octohedral, crystals. When heated by itself it evaporates, and the vapour formed by the evaporation of one molecule of the salt occupies the volume occupied by free ammonia, plus that occupied by free hydrochloric acid; and for this reason it has been suggested that the salt may be decomposed by evaporation into free hydrochloric acid and free ammonia.

Ammonia chloride is formed by adding a solution of ammonia carbonate to a solution of calcic chloride; calcic carbonate being precipitated, while the ammonia chloride remains in solution—

$$CaCl^2 + (NH^4)^2CO^3 = CO^3Ca + (NH^4Cl)^2;$$

but if the mixture of calcic carbonate and sal-ammonia be boiled, the reverse process takes place, ammonia carbonate

being carried away by the steam as fast as it is formed, while calcic chloride remains in the solution.

Iron exposed to the air becomes rusty very rapidly when moistened with a solution of sal-ammonia.

**99. Chlorocarbonic Acid** ($C O Cl^2 = 2$ vols.) is frequently called phosgene gas.

The most easy way of obtaining this gas is to pass a mixture of equal volumes of chlorine and carbonic oxide through a long glass tube exposed to bright sunshine. The mixture condenses into half its volume of a colourless gas, consisting of chloro-carbonic acid, possessing a most suffocating odour. Its density is 49.5.

The gas may be considered as carbonic acid, in which one atom of oxygen is replaced by an equivalent quantity, namely two atoms, of chlorine. In contact with moisture it is rapidly decomposed, with formation of hydrochloric and carbonic acids; $C O Cl^2 + H^2 O = C O^2 + (H Cl)^2$.

With dry ammonia phosgene forms a compound of amidogen ($N H^2$) with carbonic oxide, called urea, together with ammonia chloride—

$$(N H^3)^4 + C O Cl^2 = C O (N H^2)^2 + (N H^4 Cl)^2.$$

**100.** The action of chlorine on compounds of carbon and hydrogen is of two kinds. With some hydrocarbons it combines in the proportion of two atoms of chlorine to one molecule of the hydrocarbon. Olefiant gas affords an instance of this action, for when equal volumes of chlorine and olefiant gas are mixed in presence of water, the gases combine, forming a heavy oily liquid of the composition $C^2 H^4 Cl^2 = 2$ vols. This substance has obtained the name "Dutch liquid." It is not dissolved or acted upon by water, nor by a solution of potash in water. It boils without decomposition at about 84°C, and its vapour has a sweetish and agreeable odour not unlike that of chloroform. The liquid has a density of 1.28 at 0°C, and its vapour has a density of 49.5.

The other kind of action of chlorine on hydrocarbons is illustrated by the case of marsh gas. Two atoms of chlorine react on one molecule of the hydrocarbon, but one of these atoms of chlorine takes hydrogen out of the hydrocarbon, forming hydrochloric acid, while the other atom of chlorine takes the place of the atom of hydrogen in the hydrocarbon. Thus, a mixture of two volumes of chlorine with two volumes of marsh gas forms two volumes of hydrochloric acid, and a compound of $CH^3$ with one atom of chlorine; $CH^4 + Cl^2 = CH^3Cl + HCl$.

The compound $CH^3Cl$ is called methylic chloride. It dissolves in water, at the temperature of 14°, to the extent of several times the volume of the water; and at temperatures below 6°C it forms a crystalline compound with water. When heated to 100°C with potassic hydrate it is decomposed, the potassium combining with its chlorine, and the group $CH^3$, called methyle, taking the place of the potassium, forming methylic hydrate—

$$CH^3Cl + KHO = KCl + CH^3HO.$$

Methylic chloride can be condensed to the liquid state by the aid of a powerful frigorific mixture, and boils at −23.73.

A mixture of equal volumes of chlorine and methylic chloride is in its turn decomposed by sunshine, the action of the chlorine being an exact repetition of the process by which the chloride itself was formed: viz.

$$CH^3Cl + Cl^2 = CH^2Cl^2 + HCl.$$

This body is an oil, insoluble in water, having a density of 1.344 at 18°C, and a boiling-point of 30.5. Its vapour has the same volume as that of methylic chloride—

$$CH^2Cl^2 = 2 \text{ vols.};$$

so that the atom of chlorine has taken the place of one atom of hydrogen in methylic chloride, without disturbing the other atoms of the compound.

By repeating the action of chlorine, a still further substitu-

tion of hydrogen by chlorine can be effected in a precisely similar manner ($CH^2Cl^2 + Cl^2 = CHCl^3 + HCl$), and the compound thus obtained is the well-known

**101. Chloroform** ($CHCl^3 = 2$ vols.) This compound is prepared on a large scale by distilling spirits of wine with bleaching powder mixed with a large quantity of water. It is heavier than the compound $CH^2Cl^2$, and has a higher boiling-point, its density being 1.491 at 17°C, and its boiling-point 60.16°C. It is not acted upon by water under 100°C, nor can its chlorine be discovered by a watery solution of argentic nitrate. It is, however, dissolved by alcohol, and potash can then be mixed with it, when on the application of heat a brisk decomposition takes place, forming potassic chloride and formiate— $CHCl^3 + (HKO)^4 = CHKO^2 + (KCl)^3 + (H^2O)^2$.

Chloroform is much used for allaying temporarily the sensation of pain, an action which is termed anæsthetic. When inhaled in sufficient quantity with air, it entirely suspends the consciousness of the patient.

Its vapour is decomposed by passing through a red-hot tube, and if moisture be present hydrochloric acid is thus obtained in abundance.

**102. Carbonic Chloride** ($CCl^4 = 2$ vols.). By passing the vapour of chloroform with an excess of chlorine through a red-hot glass tube this compound is formed. Its density is 1.599, and it boils at 76.05. When potassium-amalgam is put into a solution of carbonic chloride in alcohol, the chlorine is gradually taken out of it, and replaced atom for atom by hydrogen. In this manner marsh gas can be recovered from the chloride.

The intermediate compounds $CHCl^3$, $CH^2Cl^2$, and $CH^3Cl$ are, however, formed at the same time, and the process must be considered as a substitution of one atom of chlorine at a time by hydrogen. Thus—

$$CCl^4 + H^2 = CHCl^3 + HCl,$$
$$CHCl^3 + H^2 = CH^2Cl^2 + HCl, \text{ \&c.}$$

The hydrogen must for this purpose be in the nascent state, as free hydrogen does not produce the effect.

There is also a chloride of carbon ($C^2Cl^4$) corresponding to olefiant gas, a liquid which boils at 122°C, and another formed from it at high temperatures corresponding to acetylene and having the formula $Cl^2\ Cl^2$. This protochloride is a crystalline solid which evaporates without fusion at 200°C.

Cyanogen forms three isomeric compounds with chlorine—a gaseous, a liquid, and also a solid, chloride. They are obtained by the action of chlorine on prussic acid or mercuric cyanide; $C\,N\,H + Cl^2 = C\,N\,Cl + H\,Cl$.

The solid chloride corresponds to cyanuric acid, and consists of three molecules of the gaseous chloride united in one ($C^3N^3Cl^3$).

## APPENDIX TO CHAPTER XIV.

### PROBLEMS.

95. What volume of hydrogen would be obtained by passing a litre of hydrochloric acid gas over hot metallic iron?

96. What weight of common salt would be needed for the preparation of a kilogramme of hydrochloric acid gas? What volume will the gas occupy?

97. What weight of pure "manganese" is needed for the evolution of 100 grammes of chlorine?

98. A litre of chlorine is passed with an excess of steam through a red-hot porcelain tube. What volume of oxygen is liberated, assuming that all the chlorine combines with hydrogen?

99. What weight of potassic hydrate is needed for the neutralization of 100 grammes of hydrochloric acid gas?

100. What volume of ammonia gas is required for the neutralization of 10 grammes of hydrochloric acid gas?

101. 20 grammes of an aqueous solution of hydrochloric acid were mixed with an excess of argentic nitrate. The precipitate (argentic chloride) was collected, washed, dried, and weighed. It amounted to 4.53 grammes. Calculate the per centage of hydrochloric acid in the original solution.

102. What is the weight of a litre of sal-ammonia vapour, reduced to the normal temperature and pressure?

103. A litre of phosgene gas is completely decomposed into carbonic acid and hydrochloric acid by the action of water. What is the volume of each product?

104. What volume of chlorine can be made to combine directly with a litre of olefiant gas? What is the vapour volume of the product?

105. What is the weight of a litre of chloroform vapour?

106. Suppose a litre of carbonic chloride to be decomposed by water according to the formula

$$C Cl^4 + (H^2 O)^2 = C O^2 + (H Cl)^4,$$

what volume of each product would be formed?

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# CHAPTER XV.

**103. Bromine** (Br = 80) is found in the mother liquor of sea-water in combination with sodium and potassium, and can be set free from those compounds by the action of chlorine. On a larger scale it is prepared by processes similar to those adopted for the preparation of chlorine. Bromine is a dark-red liquid of 2.966 density. It dissolves slightly in water, and the solution has the powerful odour of bromine, an odour which is even more distressing to the respiratory organs than chlorine itself. Bromine boils at 47°, and evaporates very freely at ordinary temperatures. Its vapour has a deep-

*red* colour, not unlike that of nitric peroxide. The vapour of bromine has a density equal to 80.

104. In its compounds bromine exhibits great analogy with chlorine, but it is decidedly less energetic than chlorine in its action. Thus a mixture of equal volumes of bromine vapour and hydrogen cannot be made to combine with explosion; and hydrobromic acid once formed by indirect means is more easily decomposed than hydrochloric acid. *In* proof of this it is sufficient to heat potassic bromide with strong sulphuric acid, so as to evolve hydrobromic acid, in contact with hot sulphuric acid. There is an immediate action between these two acids, liberating bromine, by decomposition of some of the hydrobromic acid: thus,

$$S O^4 H^2 + (H Br)^2 = S O^2 + (H^2 O)^2 + Br^2.$$

Bromates, such as hydric-bromate ($Br O^3 H$), can be obtained by processes similar to those employed for the preparation of chlorates. The silver salt is insoluble in water. Hypobromites such as $Br O H$ are very much like hypochlorites. The hydrogen salt is readily obtained by agitating bromine water with red mercuric oxide.

Hydrobromic acid ($Br H = 2$ vols.) is most conveniently prepared by decomposing phosphoric bromide by the action of water; $P Br^5 + (H^2O)^4 = P O^4 H^3 + (Br H)^5$.

The aqueous solution of the acid has much resemblance to hydrochloric acid, and by double decomposition with bases it forms metallic bromides analogous to the corresponding chlorides. Argentic bromide has much resemblance to the chloride. It is however less soluble in ammonia, so that when potassic bromide is added to ammonia saturated by argentic chloride, a precipitate of argentic bromide is obtained. Bromine does not, like chlorine, form a volatile compound with chromium and oxygen, so that when a bromide is distilled with potassic di-chromate and sulphuric acid, bromine vapour escapes, without carrying over any

chromium. The action of bromine on hydrocarbons is of the same kind as that of chlorine. The compound of bromine with olefiant gas ($C^2H^4Br^2$) is an oil of 2.16 density and 132°C boiling-point. It crystallizes easily. The chloride has only a density of 1.256 and 84° boiling-point; and whenever chlorine and bromine form similar liquid and volatile compounds the bromide is heavier and has a higher boiling-point than the chloride.

**Iodine** ($I=127$; $I^2=2$ vols.) is found chiefly in the mother liquor from kelp (the ashes of sea-weeds) in combination with the alkali metals. The process of its preparation is very similar to that for liberating bromine, but the iodine which is driven off condenses easily into shining black scales of 4.95 sp. gr.

Iodine is precipitated as a black powder by the action of chlorine or of bromine on a solution of an iodide, being very slightly soluble in water. The most convenient way of recovering for use iodine which has been combined with metals is by the action of nitrous acid, such as is obtained by the reduction of nitric acid in the cells of a galvanic battery.

Iodine melts at 107°C and boils at 175°C. Its vapour has a beautiful violet colour, and a density of 127. It dissolves in alcohol with a red colour, and also in a solution of potassic iodide, but its solution in carbonic sulphide has a violet colour. Free iodine forms with starch a deep blue compound, by which even the minutest traces of the element can be detected.

Two oxygen acids of iodine are known, namely, iodic acid, forming iodates such as the hydrogen salt $HIO^3$, and periodic acid, forming periodates such as

$$HIO^4 \text{ or } Na^2HIO^6.$$

**105. Anhydrous Iodic Acid** ($I^2O^5$), obtained by boiling iodine with nitric acid. It crystallizes readily from a concentrated aqueous solution. Potassic iodate is formed by fusing potassic iodide with potassic chlorate.

The argentic and barytic iodates are insoluble in water.

Iodic acid is broken up by heat into periodic acid and oxygen.

**106.** The compounds of iodine with most elements have considerable analogy with those of bromine and chlorine; but there are several elements which are unable to combine with as great a number of atoms of iodine as of bromine or chlorine. Thus phosphorus forms a pentachloride and a pentabromide, but no pentaiodide, and no very distinct compound beyond the biniodide ($P^2I^4$). Iron and copper form respectively the compounds $Fe^2Cl^6$ and $CuCl^2$, but the corresponding iodides decompose immediately into free iodine and a lower salt, in the one case ferrous and in the other cuprous iodide.

**107. Periodic Acid** (hydric periodate $IO^6H^3$) can be formed by the simultaneous action of sodic iodate and chlorine on a solution of sodic hydrate. The acid is liberated from plumbic periodate by sulphuric acid. The hydro-disodic periodate ($IO^6Na^2H$) is almost insoluble in water. There is also a more soluble dihydro-sodic periodate ($H^2NaIO^6$).

**108. Hydriodic Acid** ($IH$ = 2 vols.) is formed in small quantities by passing hydrogen and iodine through a red-hot tube. The best way to obtain the acid for use is by decomposing a mixture of iodine and phosphoric iodide by water. An aqueous solution of the acid is easily made by passing sulphuretted hydrogen through water in which iodine is suspended. The solution cannot be kept in contact with air without undergoing decomposition, and becoming red from free iodine dissolved in it. It is also decomposed by many compounds of oxygen, such as nitrous acid, in which that element is feebly combined. It is even more readily decomposed than hydrobromic acid by strong sulphuric acid. The precipitate which it forms with argentic nitrate is insoluble in ammonia. When added to a solution of mercuric chloride

it forms a brilliant scarlet precipitate of mercuric iodide. With soluble salts of lead it forms a yellow precipitate of plumbic iodide, which crystallizes from hot water in beautiful scales. A solution of palladic nitrate forms with hydriodic acid a black precipitate of palladic iodide. This reaction affords the best separation of iodine from bromine, as bromine forms a soluble salt with palladium.

**109. Nitric Iodide** is the name given to a black powder, of varying composition, obtained by the action of iodine on a solution of ammonia. It consists of ammonia of which the hydrogen is partly replaced by iodine, atom for atom, and is remarkable for the sharp detonation with which it is decomposed when rubbed or slightly pressed in the dry state. Iodine combines with olefiant gas under the influence of sunshine, forming a crystalline compound ($C^2 H^4 I^2$) corresponding to Dutch liquid.

**110.** On hydrocarbons generally iodine has no action, or a very feeble one; but the compounds $C H I^3$, $C H^2 I^2$, $C H^3 I$, can be obtained by indirect means. The first (iodoform) is obtained by the action of iodine on spirits of wine in presence of potash. It crystallizes in beautiful yellow scales, which decompose when heated by themselves, but can be slowly volatilized by a current of steam. $C H^3 I$ is called methylic iodide. It is obtained by the action of phosphoric iodide on the compound $C H^4 O$ (methylic alcohol). Methylic iodide is a heavy oil of a rather fragrant odour. Its density is 1.9, and boiling-point 44°C. When dissolved in alcohol it is decomposed by argentic nitrate; thus, $C H^3 I + N O^3 Ag = C H^3 N O^3 + I Ag$.

**Cyanic Iodide** ($C N I$) is a solid compound, which crystallizes in beautiful needles. It is easily obtained by mixing mercuric cyanide with iodine and applying gentle heat, when mercuric iodide is formed, and cyanic iodide sublimes out—

$$Hg (C N)^2 + I^4 = Hg I^2 + (C N I)^2.$$

Iodine combines with chlorine in two proportions, forming an iodous chloride (I Cl), and an iodic chloride ($I Cl^3$). In presence of an abundance of water each atom of iodine takes up five atoms of chlorine, forming iodic acid and hydrochloric acid.

111. **Fluorine** (F = 19) is not known in the free state. Hydrofluoric acid decomposes manganic binoxide with evolution of oxygen. Chlorine decomposes argentic fluoride, but if the experiment be performed in a glass vessel the glass is attacked. No compound of fluorine with oxygen is known.

112. **Hydrofluoric Acid** (H F) is prepared by distilling pure fluorspar in the state of fine powder, or ammonia fluoride, with sulphuric acid. The experiment cannot be performed in a glass vessel, as glass is dissolved by hydrofluoric acid. A platinum vessel is best suited for the purpose—

$$Ca F^2 + S O^4 H^2 = Ca S O^4 + (H F)^2.$$

The receiver should be surrounded by ice, as the acid is exceedingly volatile. The acid is commonly kept in a dilute state, in bottles composed of gutta-percha.

Its most remarkable reaction is that of forming a volatile compound of fluorine and silicon by mere contact with silica, or any silicate, such as glass—

$$Si O^2 + (H F)^4 = Si F^4 + (H^2 O)^2.$$

A glass plate covered by a varnish of bees-wax and turpentine is not attacked by the acid nor by its vapour, but if the coating be removed in some places by scratching with a needle, the vapour of hydrofluoric acid will engrave the glass along the lines thus exposed.

Hydrofluoric acid appears to be bibasic, for by double decomposition with potash it forms not only a potassium salt but also a double salt, hydro-potassic fluoride, of considerable stability ($H K F^2$). With ammonia it forms a similar double salt with great readiness. The element has, moreover, a great resemblance to oxygen in its chemical

deportment, for silicic fluoride combines with potassic fluoride, barytic fluoride, and other fluorides, forming salts, which may be compared to the salts formed by the union of silica itself with potash, &c.,

$$Si F^6 K^2, Si F^6 Ba,$$

and hydrofluosilicic acid,

$$Si F^6 H^2, \text{ like } Si O^3 H^2.$$

Fluorine forms with many other elements besides silicon compounds of acid properties; among them boric fluoride ($B F^3$).

## APPENDIX TO CHAPTER XV.

### PROBLEMS.

107. What is the weight of a cubic centimeter of bromine vapour at 150°C and 760 mm.?

108. What weight of bromine is contained in a liter of hydrobromic acid gas?

109. What volume of hydriodic acid gas could be prepared from ten grammes of iodine?

110. Six grammes of manganic peroxide are boiled with an excess of strong hydrochloric acid. All the chlorine thus evolved is led into a solution of potassic iodide, care being taken to employ more of this iodide than the chlorine can decompose. What weight of iodine is liberated?

111. What weight of calcic sulphate could be obtained by the action of sulphuric acid on 100 grammes of calcic carbonate?

# CHAPTER XVI.

**113. Sulphur** ($S^2$, $S=32$) is found in yellow crystals in several volcanic districts, mixed with strontic sulphate, &c. It is also obtained by heating pyrites, a ferric persulphide which occurs in many parts of the world, and which parts with one-third of its sulphur at a high temperature. It is introduced into commerce in broken lumps, partly also in the form of sticks, partly in the form of a powder called flowers of sulphur. The sticks are remarkable for the facility with which they crack when gently heated, even by the hand. The flowers of sulphur are made by boiling sulphur in an iron vessel, and allowing the vapour to pass into a large chamber, where it condenses in small particles, and falls to the ground. Sulphur presents several allotropic modifications, which are distinguished from one another by their density, their melting-point, their crystalline form or state of aggregation, and their solubility.

Thus, carbonic sulphide dissolves about 75 per cent. of flowers of sulphur, the remainder being of a variety which is not soluble; and the solution deposits on evaporation clear octohedral crystals, of 2.05 density and 114.5°C melting-point. When sulphur is melted by itself, and a hole made in the crust which forms on its surface before the whole mass has solidified, the liquid portion can be poured out, leaving a number of clear needle-shaped crystals attached to the crust. This prismatic sulphur has only a density of 1.98, and, according to Brodie, it melts at 120°C. The clear prismatic crystals gradually become opaque by keeping, at a low temperature, and they are then supposed to have undergone a

change in the state of aggregation of their particles. According to Regnault the same transformation takes place rapidly, and with elevation of temperature, when clear prismatic crystals are immersed in carbonic sulphide saturated with octohedral sulphur; and on the other hand, clear octohedral crystals become opaque when heated to a temperature of about 105°C, by passing over into an aggregate of small prismatic crystals.

When sulphur is first melted it forms a pale yellow very mobile liquid, but in proportion as it is heated to a higher temperature does its colour become darker, and its consistency thicker, until at about 250°C it is an opaque mass, so nearly solid that it cannot be poured out of the vessel containing it. At still higher temperatures it again becomes perfectly liquid. If poured into cold water in this state it remains in a soft and plastic state after cooling, and can be drawn into threads. It boils at 490°C, forming a yellowish red vapour, and metallic iron or copper burns in this vapour with great intensity.

The vapour of sulphur has been found to possess at the temperature of 500°C a density corresponding to $S^6 = 2$ vols.; but at a temperature of 1000°C it has density proportional to its atomic weight, viz. 32, so that there are then two atoms of sulphur in two volumes, $S^2 = 2$ vols.

Sulphur dissolves in a solution of caustic potash, forming two compounds—potassic sulphide and hyposulphite—

$$S^4 + (H\,K\,O)^6 = (S\,K^2)^2 + S^2\,O^3\,K^2 + (H^2\,O)^3.$$

When melted with potash at a high temperature it forms a mixture of potassic sulphide and sulphate—

$$S^4 + (H\,K\,O)^8 = (S\,K^2)^3 + S\,O^4\,K^2 + (H^2\,O)^4.$$

In each case the sulphide combines with several atoms of sulphur, forming a potassic polysulphide, such as $S^5\,K^2$.

**114. Sulphuretted Hydrogen** ($S\,H^2 = 2$ vols.) Sulphur combines slowly with hydrogen at high temperatures,

forming sulphuretted hydrogen gas. The compound is usually made by dissolving ferrous sulphide in dilute sulphuric acid—

$$Fe\,S + S\,O^4\,H^2 + Aq = S\,H^2 + S\,O^4\,Fe + Aq;$$

or else by dissolving native antimonious sulphide (in lumps) in strong hydrochloric acid, by the aid of heat. The evolution of the gas ceases as soon as the source of heat is withdrawn—

$$Sb^2\,S^3 + (H\,Cl)^6 = (Sb\,Cl^3)^2 + (H^2\,S)^3.$$

The gas has a most fœtid smell when present even in the proportion of one per cent. of the air, and produces poisonous effects when inhaled in quantity. Its density is 17. A pressure of about 16 atmospheres is sufficient to liquefy it at the temperature of 15°C. The gas burns with a pale blue flame, two volumes of it combining with three volumes of oxygen, forming sulphurous acid and water. Water at 0°C dissolves 4.37 times its volume of the gas, at 10°C about 3.5 volumes, and 2.9 at 20°C. The solution is gradually decomposed by contact with the air, depositing its sulphur.

Potassium heated in sulphuretted hydrogen gas decomposes it with evolution of hydrogen, forming a compound called potassic sulph-hydrate—

$$S\,H^2 + K = S\,H\,K + H.$$

The second atom of sulphur can also be replaced by potassium, forming potassic sulphide—

$$S\,H\,K + K = S\,K^2 + H.$$

These same compounds are formed by the action of sulphuretted hydrogen on a solution of potassic hydrate. An excess of the gas forms potassic sulph-hydrate, but when this is mixed with an equivalent quantity of potassic hydrate the mixture is found to possess the properties of potassic sulphide; $S\,H\,K + O\,H\,K = S\,K^2 + O\,H^2$.

Sulphuretted hydrogen reacts in a similar manner upon a great many other metallic oxides, replacing their oxygen atom for atom by sulphur, and the sulphides thus formed

serve by their peculiar properties for the detection of many metals when present in a solution.

**115.** Sulphuretted hydrogen is usually passed through any solution which has to be investigated for metals, and there are eleven common metals which form insoluble sulphides under this treatment, if the solution contain free acid. These metals are arsenic, antimony, tin, gold, platinum, silver, mercury, lead, bismuth, copper, and cadmium. The first five of these dissolve in ammonia sulphide, while the remaining six are not soluble. Iron, uranium, chromium, aluminium, cobalt, manganese, nickel, and zinc are thrown down by sulphuretted hydrogen, in presence of ammonia sufficient to neutralize all the acids present; but of these eight, two, viz. chromium and aluminium, do not combine with sulphur in the process of precipitation.

The remaining common metals, viz. barium, strontium, calcium, magnesium, potassium, and sodium, form sulphides which are soluble in water; and they accordingly remain in the solution after the precipitation of the previous groups by sulphuretted hydrogen in the acid liquid, and by ammonia sulphide in the alkaline liquid.

Sulphuretted hydrogen acts upon some oxides as a reducing agent, without giving them sulphur in lieu of the oxygen which it removes. The commonest cases of this action are those of chromic acid and ferric oxide. In presence of free acid these oxides are reduced with deposition of sulphur, chromic oxide being formed from the one and ferrous oxide from the other—

$$(CrO^3)^2 + (H^2S)^3 = Cr^2O^3 + (H^2O)^3 + S^3.$$

$$Fe^2O^3 + H^2S = (FeO)^2 + H^2O + S.$$

Sulphurous acid, in presence of water, is also decomposed by sulphuretted hydrogen—

$$SO^2 + (H^2S)^2 = S^3 + (H^2O)^2.$$

Strong sulphuric acid is decomposed by sulphuretted hydrogen, sulphurous acid being given off.

An exceedingly delicate and beautiful test for sulphuretted hydrogen is sodic nitroprusside with an excess of ammonia. Sulphuretted hydrogen gives a deep purple colour to the mixture.

**Hydric Persulphide** ($H^2S^2$)—an oily precipitate—is formed when sodic bisulphide is poured gradually into hydrochloric acid. When separated from the liquid this precipitate gradually decomposes, giving off sulphuretted hydrogen and leaving sulphur.

**116. Sulphurous Acid** ($SO^3 = 2$ vols.) is the sole product of the combustion of sulphur in the atmosphere. For manufacturing purposes it is obtained mixed with nitrogen by burning pyrites ($FeS^2$). On a small scale it is best prepared by heating mercury or copper with strong sulphuric acid; $Hg + (SO^4H^2)^2 = SO^4Hg + SO^2 + H^2O$.

Charcoal powder is sometimes substituted for the metal, but in that case the gas which comes off is mixed with carbonic acid.

The gas is well known for its peculiar pungent odour. Its density is exactly double that of oxygen (32), for the gas occupies the same volume as the oxygen from which it is made. It dissolves readily in water: its coefficient of absorption being at 0°C 68.86; at 10°C 51.38, and at 20°C 36.22. It dissolves still more readily in alcohol. A pressure of about two atmospheres is sufficient to liquefy the gas at 15°, forming a limpid fluid of 1.42 density.

The salts of sulphurous acid are called sulphites. They exhibit considerable analogy of constitution with the carbonates, being of two classes—simple sulphites (such as the potassic sulphite $SO^3K^2$), and double sulphites (such as $SO^3KH$). They are decomposed by hydrochloric, sulphuric, or nitric acid, the sulphurous acid being expelled; but they

are not decomposed by carbonic acid. Sulphurous acid is used for bleaching woollen or silken fabrics, and it is an efficacious agent for preventing putrefaction and fermentation. Its silver salt is decomposed by heat in presence of water, metallic silver being deposited, and hydric sulphate remaining in the solution—

$$SO^2 + Ag^2O + H^2O = SO^4H^2 + Ag^2.$$

Its aqueous solution gradually absorbs oxygen from the air, and is rapidly oxidized by chlorine, iodine, or nitrous acid. At high temperatures sulphurous acid absorbs oxygen, forming sulphuric acid, and it is therefore evident that if sulphur were burnt at a high temperature the product would no longer be sulphurous acid, but sulphuric acid. It is deprived of its oxygen by nascent hydrogen, and at the same time supplied with two atoms of hydrogen in place of the oxygen—

$$SO^2 + H^6 = SH^2 + (OH^2)^2.$$

Sulphurous acid is absorbed by plumbic peroxide, forming plumbic sulphate; $SO^2 + PbO^2 = SO^4Pb$.

117. **Hydric Sulphate** ($SO^4H^2 = 4$ vols.), commonly called sulphuric acid. This important acid salt is prepared by the action of sulphurous acid on nitrous acid in presence of steam. Every molecule of sulphurous acid requires two molecules of nitrous acid, from which it liberates nitric oxide—

$$SO^2 + (NO^2H)^2 = SO^4H^2 + (NO)^2.$$

The nitric oxide liberated at the end of the reaction is made to serve again by putting moist air in contact with it, so that it takes up oxygen and water and reproduces nitrous acid; $(NO)^2 + O + H^2O = (NO^2H)^2$; and by supplying air and allowing the substances time to act on one another a small quantity of nitric oxide is thus made to prepare a large quantity of sulphuric acid. The manufacture is carried on in vast leaden chambers, constantly supplied at one end with air partially deprived of its free oxygen by burning sulphur or pyrites, and with this air the vapour of

strong nitric acid. Steam is blown into the chamber to aid the combination, and the residual nitrogen and nitric oxide escape at the further end by a flue. To recover the nitric oxide this air is sometimes made to pass over a large surface of coke, wetted with strong sulphuric acid.

The dilute acid thus obtained is evaporated at first in leaden pans; but the evaporation is completed in platinum or glass retorts; the water which is distilled off, together with a small quantity of acid carried over as spray, being collected for use in the chambers. The acid thus obtained, commonly called oil of vitriol, is of the composition $SO^4H^2$, and density 1.842. It boils at 327°C. It is very liable to contain a little plumbic sulphate in solution, and ought to be distilled in a platinum retort if required in a state of purity.

By limiting the temperature during evaporation to 205°C an acid is obtained of density 1.78, and consisting of $SO^4H^2OH^2$, which crystallizes at temperatures below 9°C. By evaporating a dilute acid at 100° a compound is obtained $SO^4H^2(OH^2)^2$, of density 1.62.

**118. Anhydrous Sulphuric Acid** ($SO^3$ = 2 vols.) can be obtained by decomposing oil of vitriol by anhydrous phosphoric acid, or by heating sodic disulphate ($Na^2S^2O^7$), $SO^3$ passes over while the normal sodic sulphate $Na^2SO^7$ remains behind. The acid can also be obtained by distilling ferric oxy-disulphate; $Fe^2O(SO^4)^2 = Fe^2O^3 + (SO^3)^2$. It is a white solid, similar in appearance to asbestos. Its density is 1.9. It boils a little above 50°C, and evaporates in large quantities at the common atmospheric temperatures, forming dense white fumes, by combining with the moisture of the air.

When brought in contact with a small quantity of water, it combines with explosive violence, giving off a great deal of heat. It decomposes organic bodies very rapidly, liberating carbon. It also combines with nitric oxide, forming the

compound $SO^4N$. With dry ammonia it combines very slowly, but the addition of water causes instant combination.

## APPENDIX TO CHAPTER XVI.

### PROBLEMS.

112. What weight of sulphur is contained in a litre of sulphuretted hydrogen?

113. What volume of oxygen is required for the combustion of a cubic centimeter of sulphuretted hydrogen? What is the volume of each product?

114. What weight of antimonic sulphide is required for the preparation of 500 grammes of sulphuretted hydrogen?

115. What volume of sulphurous acid is formed by the combustion of 10 grammes of sulphur?

116. What weight of sulphurous acid is required for the neutralization of 100 grammes of potassic hydrate?

117. Ascertain from the tables the percentage of sulphuric acid in a solution of 1.6 density, and calculate what weight of that solution must be used for the neutralization of 10 grammes of lime (Ca O).

118. What volume of air is needed for the complete oxidation of a kilogramme of sulphur?

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# CHAPTER XVII.

**119. Sulphamic Acid** ($SO^2(NH^2)(HO)$). The compound formed by the slow combination of ammonia with an

hydrous sulphuric acid, is the ammonia salt of a peculiar acid having the above composition. The acid does not precipitate salts of baryta, but by taking up the element of one molecule of water it is transformed into hydrammonic sulphate—

$$S O^3 N H^3 + H^2 O = S O^4 H (N H^4).$$

**Sulphamide** ($S O^2 (N H^2)^2$) is formed by the action of ammonia on chlorosulphuric acid—

$$S O^2 Cl^2 + (N H^3)^2 = S O^2 (N H^2)^2 + (H Cl)^2.$$

The hydrochloric acid which is formed unites immediately with ammonia. This amide may be compared to urea, which is formed by a similar reaction from chloro-carbonic acid and ammonia.

120. **Carbamic Acid** ($CO\ NH^2\ HO$) is an acid which stands to carbamide in the same relation in which sulphamic acid stands to sulphamide, but it is chiefly known in combination with organic bodies.

There is a remarkable compound containing the elements of anhydrous sulphuric acid added to those of hydric sulphate. It is known by the name of fuming sulphuric acid. Its composition is represented by the formula $S^2 O^7 H^2$. It may be considered as a compound of $S O^3$ and $S O^4 H^2$, for at a very gentle heat it can be separated into these two bodies, $S O^3$ distilling over and $S O^4 H^2$ remaining behind. The fuming acid is made by distilling ferric oxy-disulphate ($Fe^2 O^3 (S O^3)^2$) and collecting the anhydrous acid which comes over in receivers containing some sulphuric acid.

The vapour of sulphuric acid (hydric sulphate) has a density of 24.5, which corresponds to $S O^4 H^2 = 4$ vols. There are strong reasons for believing that it contains two molecules ($S O^3$ and $H^2O$) uncombined with one another, for even below its boiling-point the acid loses water, and steam has been diffused out of the vapour of the acid.

When passed through a red-hot tube sulphuric acid vapour is in part decomposed into sulphurous acid and oxygen gas.

The acid is also decomposed by contact with organic matter, especially if metals capable of combining with sulphur be present.

Great heat is evolved when sulphuric acid is mixed with water, and most organic bodies containing the elements of water are decomposed by contact with the concentrated acid. Thus sugar is blackened and destroyed by it; even alcohol is charred and burnt by heating with abundance of the strong acid.

Sulphuric acid forms with barium a salt perfectly insoluble in water or in hydrochloric acid, and its presence is best detected by this test. The barytic sulphate is reduced by charcoal at a red heat, forming barytic sulphide, which gives off sulphuretted hydrogen by the action of acids—

$$S\,O^4\,Ba + C^4 = S\,Ba + (C\,O)^4.$$

**121. Hyposulphurous Acid** ($S^2\,O^2$) is only known in combination with bases in the hyposulphites. Its sodium salt is much used by photographers, as it dissolves argentic iodide. When the hydrogen salt $H^2\,S^2\,O^3$ is liberated by hydrochloric acid from a solution of this salt it decomposes almost immediately, depositing sulphur and giving off sulphurous acid. The silver salt of hyposulphurous acid decomposes rapidly, forming sulphuric acid and argentic sulphide—

$$S^2\,O^3\,Ag^2 + H^2\,O = S\,Ag^2 + S\,O^4\,H^2.$$

**Hyposulphuric Acid** ($S^2\,O^6$) is prepared in solution by adding dilute sulphuric acid to the solution of barytic hyposulphate so as to precipitate the baryta from it without leaving any sulphuric acid in excess. The dilute acid is evaporated in vacuo over sulphuric acid. Its baryta salt ($S^2\,O^6\,Ba$) is remarkable for being soluble in water.

When the salt is heated by itself it decomposes, giving off sulphurous acid and leaving barytic sulphate. A similar decomposition occurs when a solution of barytic hyposulphate

is heated with hydrochloric acid; barytic sulphate is deposited while sulphurous acid is liberated.

The other three acids of sulphur—viz. monosulphuretted hyposulphuric acid ($S^3O^6H^2$), disulphuretted hyposulphuric acid ($S^4O^6H^2$), and trisulphuretted hyposulphuric acid ($S^5O^6H^2$)—have been but little studied.

**122. Ammonia Sulphide** ($S(NH^4)^2$) can be obtained by mixing one volume of sulphuretted hydrogen with two volumes of ammonia, and passing the mixture into a tube cooled to $-18°$, or more easily by heating a mixture of sal-ammonia and potassic sulphide and condensing at $-18°C$. It is a colourless salt which decomposes at $0°C$, giving off ammonia and leaving $SH(NH^4)$ hydrammonic sulphide.

A solution of the compound is usually prepared by dividing a given quantity of ammonia into two equal portions, saturating one portion by sulphuretted hydrogen, thereby forming $SH(NH^4)$, and then mixing it with the other portion. The solution is exceedingly alkaline, and rapidly turns yellow in contact with the air, by absorbing oxygen, and forming a mixture of ammonia and ammonia persulphide, which decomposes further, forming tersulphide and hyposulphite.

Sulphuric acid forms two salts with ammonia—the normal sulphate $SO^4(NH^4)^2$, which crystallizes in the same form as the normal potassic sulphate $SO^4K^2$. The other compound is the double sulphate $SO^4H(NH^4)$. Sulphurous acid forms two similar ammonia salts—$SO^3(NH^4)^2$ and $SO^3H(NH^4)$.

**123. Carbonic Sulphide** ($CS^2$ = 2 vols.) This compound is the analogue of carbonic acid, and it is sometimes called sulpho-carbonic acid. It is made by burning red-hot carbon in sulphur vapour. It is an oil, insoluble in water, and of a density of 1.26. It boils at 45°C, and its vapour has the same volume as carbonic acid, and accordingly a density of 38. Its odour is exceedingly offensive, and is said to produce very

injurious effects upon persons frequently exposed to it. It burns with a pale blue flame. Carbonic sulphide combines with the sulphides of many basic metals, such as potassic sulphide, forming compounds analogous to those which carbonic acid forms on combining with basic oxides. These compounds are called sulpho-carbonates. They are decomposed in presence of water by strong acids, a compound of carbonic sulphide with sulphuretted hydrogen being formed. This compound—

**124.** $CS^3H^2$ is the true hydric sulpho-carbonate or sulpho-carbonate of hydrogen. Ammonia solution decomposes carbonic sulphide, forming sulphuretted hydrogen and an acid analogous to cyanic acid, and differing from it only by having an atom of sulphur in place of the atom of oxygen in cyanic acid. This sulphur acid is a valuable re-agent. It is called sulpho-cyanic acid.

$$CS^2 + NH^3 = CNSH + SH^2.$$

These products combine with ammonia, forming ammonia sulpho-cyanate and ammonia sulphide. Ammonia sulpho-cyanate forms a deep blood-red compound when mixed with a solution of ferric salt. The red compound consists of ferric sulpho-cyanate ($Fe^2(CNS)^6$).

There are two chlorides of sulphur—hyposulphurous subchloride ($S^2Cl^2$ = 2 vols.), obtained by passing dry chlorine into flowers of sulphur, and distilling off from the sulphur which is dissolved. It is a yellow liquid of unpleasant odour, and emits fumes in moist air. Its density is 1.68, and it boils without decomposition at 138°C. In contact with water it is decomposed, forming hydrochloric acid, while the sulphur is partly deposited in the free state, partly in combination with oxygen as sulphurous acid.

Hyposulphurous chloride ($SCl^2$) is obtained by saturating the subchloride with chlorine, and distilling in a stream of chlorine. The compound gives off chlorine when heated,

and is partially reduced to subchloride. It is decomposed by water like the subchloride.

**125. Chlorosulphuric Acid** ($S O^2 Cl^2$ = 2 vols.) is formed by the combination of equal volumes of chlorine and sulphurous acid. A more convenient way of making it is by decomposing sulphuric acid by an excess of phosphoric chloride—

$$S O^4 H^2 + (P Cl^5)^2 = S O^2 Cl^2 + (P O Cl^3) + (H Cl)^2.$$

The liquid boils at 80°, and has a density of 1.68. It is decomposed gradually by water, forming one molecule of sulphuric acid and two molecules of hydrochloric acid—

$$S O^2 Cl^2 + (H^2 O)^2 = S O^4 H^2 + (H Cl)^2.$$

It is to be considered as sulphuric acid in which $(H O)^2$ is replaced by $Cl^2$.

Chlorohydrated sulphuric acid ($S O^2 Cl H O$) is the first product of the action of phosphoric chloride on sulphuric acid; $S O^4 H^2 + P Cl^5 = S O^3 H Cl + P O Cl^3$; and in its composition it is intermediate between hydrated sulphuric acid and chlorosulphuric acid. It is also formed by the action of hydrochloric acid gas on anhydrous sulphuric acid. The anhydrous acid does not combine with more than one molecule of hydrochloric acid, and only sluggishly with so much—

$$S O^3 + H Cl = S O^2 Cl (H O).$$

It appears to form salts, but owing to their instability they have been but little studied. The soda salt is obtained by the combination of sodic chloride with anhydrous sulphuric acid.

**126. Selenium** (Se = 79.5). This rare element is chiefly of interest from its analogy with sulphur. The element can be reduced from its oxide ($Se O^2$), called selenious acid, by the action of sulphurous acid in solution. It goes down in the form of a red powder, which can be melted together at a temperature somewhat over 100°C. It is a dark brown substance of 4.3 density, very friable, it

evaporates at a higher temperature than sulphur, and produces, even when present in air in small quantities, an odour like horse-radish. Selenium combines in two proportions with oxygen, forming selenious acid and selenic acid, corresponding to sulphurous and sulphuric acids. It is not improbable that the volatile substance which is formed at the same time with selenious acid by the combustion of selenium in the air may be a lower oxide of selenium.

Selenious acid is precipitated from its solutions by sulphuretted hydrogen—

$$Se\,O^2 + (H^2S)^2 = Se\,S^2 + (H^2O)^2;$$

and the selenious sulphide so obtained is a sulphur acid, and forms numerous sulphur salts called sulpho-selenites. Selenic acid has great resemblance with sulphuric acid, and forms many salts, such as $Na^2\,Se\,O^4$, which are undistinguishable, in their crystalline form, from the corresponding sulphates. Barytic seleniate is insoluble in water, but dissolves with evolution of chlorine in boiling hydrochloric acid, and can thereby be distinguished from barytic sulphate—

$$Se\,O^4Ba + (H\,Cl)^4 = Se\,O^2 + Ba\,Cl^2 + Cl^2 + (H^2O)^2.$$

Seleniuretted hydrogen ($Se\,H^2$ = 2 vols.) is prepared in a similar manner to sulphuretted hydrogen, and shews considerable resemblance with that body in its action on solutions of metallic salts.

**127. Tellurium** (Te = 129) is a rare biatomic element, of metallic appearance, and of a density of about 6.2. It melts at a higher temperature than lead, and can be volatilized at a red heat. Tellurium conducts electricity, whereas sulphur and selenium are non-conductors. It can be precipitated by zinc from solutions, like a weak metal. In spite of these facts chemists are agreed to place tellurium in the same family with oxygen, sulphur, and selenium, on account of the close analogy which its compounds exhibit with those of selenium.

Tellurous acid dissolves in hydrochloric acid, but very slightly in water; it is precipitated from acid solutions by sulphuretted hydrogen—

$$Te\,O^2 + (H^2\,S)^2 = Te\,S^2 + (H^2\,O)^2;$$

and tellurium is reduced from it by a solution of sulphurous acid. Telluric acid forms with baryta a salt which, although insoluble in water, is soluble in nitric acid, and tellurium is thus separated from selenium.

Hydric tellurate crystallizes readily in combination with two molecules of water—

$$Te\,O^4\,H^2\,(O\,H^2)^2.$$

The anhydrous acid ($Te\,O^3$) is obtained by heating the hydrogen salt. It is insoluble in water, and dissolves with great difficulty in potash.

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# CHAPTER XVIII.

**128. Phosphorus** ($P = 31$, $P^4 = 2$ vols.) Phosphorus is usually made from bone-earth (the ashes of bones). This material consists mainly of calcic phosphate ($P^2O^8\,Ca^3$), and when it is acted upon by sulphuric acid and water a part of the lime is removed as calcic sulphate, which can be filtered off from the soluble double-phosphate, commonly called superphosphate of lime—

$$P^2\,O^8\,Ca^3 + (S\,O^4\,H^2)^2 = P^2\,O^8\,Ca\,H^4 + (S\,O^4\,Ca)^2.$$

The solution is evaporated to dryness with charcoal and the mixture heated in stoneware retorts. Carbonic oxide is formed, and phosphorus distills over, and is collected under water to protect it from the air. Calcic phosphate remains in the retort.

$$(P^2\,O^8\,Ca\,H^4)^3 + C^{10} = P^4 + (C\,O)^{10} + P^2\,O^8\,Ca^3 + (H^2\,O)^6.$$

Phosphorus is generally cast into sticks, and sent out for

sale under water in tin cases. It is a clear colourless substance of 1.83 density. It melts at 45°C, and is easily cast into moulds under water, as it does not dissolve in water. A stick of phosphorus when exposed in the air emits a faint light, visible in a dark room; and when it is gently rubbed against a hard surface luminous marks are left. The experiment is however exceedingly dangerous, as phosphorus catches fire when rubbed, and produces painful burns which heal with difficulty. It should always be cut under water.

In summer weather it has the consistency of wax; in winter it is brittle. It boils at 290°C, and its vapour has a density of 62, proving that two atoms of phosphorus occupy the same volume as one atom of hydrogen. Phosphorus dissolves in large quantities in carbonic sulphide, and can be obtained in crystals from that solution. It is dissolved by hot aqueous solutions of potash, soda, lime, &c., and on dissolving in them it gives off a gas which catches fire by mere contact with air, and burns with a white flame, forming phosphoric acid and water. Another part of the phosphorus is found in the solution, in the form of potassic hypophosphite—

$$P^4 + (H^2 O H K O)^3 = P H^3 + (P O^2 H^2 K)^3;$$

other products are formed at the same time.

**129.** When phosphorus is heated to a temperature of 240° it gradually forms a red deposit, and if the heat be continued long enough nearly all the phosphorus is transformed into this red substance. At a still higher temperature the red powder evaporates, and its vapour on condensation yields common clear phosphorus, similar to that obtained by distilling the clear phosphorus itself. The red powder is nothing else than phosphorus in an allotropic state. It is most conveniently separated from common phosphorus by carbonic sulphide, in which red phosphorus is quite insoluble. The most convenient way to prepare red

phosphorus in small quantities is that discovered by Brodie, viz. to dissolve some phosphorus in carbonic sulphide, with a small quantity of iodine, and heat the solution to 100°C in a sealed-up tube for some time. The red phosphorus is then deposited from the liquid in proportion as it is formed.

Red phosphorus is less active chemically than clear phosphorus, and all differences between the two varieties are connected with this one. Red phosphorus requires a much higher temperature for its ignition than that at which clear phosphorus kindles into flame. The heat of combustion of clear phosphorus is to that of red phosphorus in the proportion of 1.15 to 1. The specific heat of red phosphorus is also less than that of the clear variety, the former being 0.1700, the latter 0.1887. The density of red phosphorus is usually about 2.1.

A stick of clear phosphorus decomposes cupric sulphate when immersed in a solution of the salt, becoming coated with metallic copper, while the phosphorus dissolves as phosphoric acid. Red phosphorus made by heat has no such action. Caustic soda is used by the manufacturers of red phosphorus to purify it from clear phosphorus.

The red phosphorus made by the action of iodine exhibits an interesting anomaly when distilled, for its vapour condenses in great part in the form of red phosphorus. This result is due to the presence of a trace of iodine, which remains in the phosphorus and evaporates with it. This iodine causes the change of clear phosphorus into red in proportion as it condenses from the vapour. Red phosphorus does not emit light when exposed to the air, and does not undergo the slow combustion which occurs with clear phosphorus, and to which the phosphorescence is owing.

Both kinds of phosphorus burn in oxygen, sulphur, or chlorine, and form two compounds with each of these elements, viz. $P^2O^3$, $P^2O^5$; $P^2S^3$, $P^2S^5$; $PCl^3$, $PCl^5$. Some

compounds with less sulphur are also known. The element can also be obtained in combination with hydrogen and the metals; for instance, phosphuretted hydrogen is $PH^3$, and there are two cupric phosphides, $P^2Cu^3$ and $PCu^3$.

**130. Anhydrous Phosphoric Acid** ($P^2O^5$) is made by burning phosphorus in dry air, taking care to supply the air in abundance to the flame. It is a snow-like powder, and is volatile at a high temperature. It combines with water very energetically, and takes it from most compounds in which the elements of water are contained. Each molecule of the anhydrous acid combines with three molecules of water, forming two molecules of the hydrated acid $PO^4H^3$—

$$P^2O^5 + (H^2O)^3 = (PO^4H^3)^2;$$

and this water can be but partially expelled by heat. By exposing the hydrate to a red heat in a platinum dish, a vitreous-looking mass is obtained, which is generally called glacial phosphoric acid, and which retains one-third of the hydrogen of the original salt—

$$PO^4H^3 = PO^3H + H^2O.$$

A recently prepared solution of glacial phosphoric in cold water carefully neutralized by ammonia gives a white precipitate with argentic nitrate: thus,

$$PO^3NH^4 + NO^3Ag = PO^3Ag + NO^3NH^4;$$

but if the solution be boiled for some time with plenty of water, and then neutralized and precipitated by argentic nitrate, it gives a bright yellow precipitate containing three times as much silver as the white precipitate—

$$PO^4(NH^4)^3 + (NO^3Ag)^3 = PO^4Ag^3 + (NO^3NH^4)^3.$$

**131. Trihydric Phosphate,** commonly called phosphoric acid ($PO^4H^3$), is most conveniently prepared by dissolving phosphorus in dilute nitric acid, with the aid of heat. The operation is usually performed in a glass retort, provided with a condenser, as a good deal of nitric acid evaporates during the operation with the nitrous acid. The phosphorus dis-

solves gradually, but to ensure its being fully oxidised some nitric acid should be added after the phosphorous has disappeared, and the whole then evaporated to a syrupy consistence.

Phosphoric acid can also be prepared from bone-earth. For that purpose the bone-earth is decomposed by sulphuric acid, as for the preparation of phosphorus, and the filtered solution of hydrocalcic phosphate is neutralized by ammonia. The effect of this is to form triammonic phosphate, which remains in the solution, and to precipitate calcic phosphate—

$$((PO^4)^2\,Ca\,H^4)^3 + (N\,H^3)^{12} = (P\,O^4)^2\,Ca^3 + (P\,O^4\,(N\,H^4)^3)^4.$$

The solution is filtered off from the precipitate of calcic phosphate, evaporated to dryness and heated to redness in a platinum vessel. The ammonia is entirely expelled by the heat, and the residue is glacial phosphoric acid, ready for solution.

Phosphoric acid is tribasic. With potassium it forms two double salts, hydro-dipotassic phosphate $H\,K^2\,P\,O^4$, and dihydro-potassic phosphate $H^2\,K\,P\,O^4$, besides the normal salt $K^3\,P\,O^4$. There are similar salts with sodium. The force with which the first atom of hydrogen is replaced is greater than that with which the second is replaced, and the third atom of potassium is taken up so feebly that the presence even of carbonic acid is sufficient to prevent potash from reacting on the hydro-dipotassic sulphate.

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# CHAPTER XIX.

**132.** Di-hydro-sodic phosphate ($H^2\,Na\,P\,O^4$) is decidedly acid to test-paper, and it expels carbonic acid from sodic carbonate with brisk effervescence, forming the hydrodisodic, or common phosphate $H\,Na^2\,P\,O^4$. But this common

phosphate, containing two atoms of sodium and one of unreplaced hydrogen, is no longer acid to test-paper, indeed it is faintly alkaline. The normal phosphate, containing three atoms of sodium, is perfectly alkaline to test-paper, and when dissolved in water it absorbs carbonic acid from the air, like caustic soda.

Although the molecule of phosphoric acid combines with three molecules of soda it must be admitted only to neutralize two molecules, as the alkaline properties of the third molecule of soda are maintained in the normal salt.

The basic hydrogen of hydric phosphate is sometimes replaced partly by one basic metal, partly by another; thus, a common salt, called microcosmic salt, contains sodium, ammonium, and hydrogen, combined as basylous metals in one molecule of the phosphate. Its formula is—

$$PO^4NaNH^4H.$$

When phosphoric acid is neutralized by ammonia it can be fully precipitated from its solution by the addition of magnesic sulphate. The precipitate consists of a molecule of the hydrogen salt, in which two atoms of hydrogen are replaced by one atom of magnesium, while the third atom of hydrogen is replaced by ammonium ($PO^4MgNH^4$).

Phosphoric acid forms with ferric oxide a salt which is valuable for being insoluble in acetic acid. The salt is easily obtained by precipitating a soluble phosphate by ferric chloride. Its composition is represented by the formula $PO^4Fe$, or a multiple of that. In presence of free mineral acids, phosphoric acid can be detected by the yellow precipitate which it forms with ammonic nitro-molybdate.

Common phosphoric acid does not coagulate albumen. And in this respect it resembles pyrophosphoric acid ($H^4P^2O^7$), and differs from metaphosphoric acid $(HPO^3)^n$.

**133. Tetrahydric Diphosphate,** commonly called pyrophosphoric acid ($P^2O^7H^4$). By heating common hydrodi-

sodic phosphate to a bright red heat the salt is deprived of its basic water, and transformed into the pyrophosphate $P^2O^7Na^4$. Phosphates of this constitution can be distinguished from common phosphates partly by the lesser solubility of the sodium salt ($Na^4P^2O^7$), partly also by the white colour of the silver salt ($P^2O^7Ag^4$). The tetrahydric diphosphate resembles common phosphates, however, in the circumstance that when added to barytic chloride, or to argentic nitrate, it produces no precipitate; the neutralization by an alkali is necessary for the formation of either precipitate.

**Metaphosphoric Acid** $(PO^3H)^n$. The glacial acid has this composition, but there appear to be several varieties of it, differing from one another in molecular weight, some being higher multiples of the formula $PO^3H$ than others.

Pyrophosphates, as well as these metaphosphates, are converted into common tribasic salt by long boiling with water, in an acid liquid; or by fusion with an excess of caustic alkali.

**134. Phosphorous Acid** ($P^2O^3$) can be obtained by burning a piece of phosphorus in a glass tube, with very limited supply of dry air. It is more volatile than phosphoric acid. It dissolves readily in water, forming hydric phosphite ($PO^3H^3$); but when the solution is evaporated to dryness, and heated, for the purpose of driving off the water, the acid is decomposed, evolving phosphuretted hydrogen, and forming phosphoric acid.

A solution of phosphorous acid is most conveniently prepared by decomposing phosphorous chloride by water—

$$PCl^3 + (H^2O)^3 = PO^3H^3 + (HCl)^3.$$

The hydrochloric acid is expelled by evaporation. Phosphorous acid is bibasic; for no more than two of its atoms of hydrogen can be replaced by potassium, or sodium, or other basic metals; and in the double phosphites only one-third of the hydrogen of the acid is replaced by one metal.

It reduces silver, gold, or mercury from solutions of their salts. With mercuric chloride the first action consists in precipitating calomel—

$$PO^3H^3 + (HgCl^2)^2 + H^2O = PO^4H^3 + Hg^2Cl^2 + (HCl)^2.$$

**Hypophosphorous Acid** ($PO^2H^3$). It was mentioned above that a salt of this acid is formed by boiling phosphorus in potash or baryta, &c. When baryta is used, all the phosphoric and phosphorous acids formed go down in combination with baryta; barytic hypophosphite alone remaining in solution with the excess of base. The acid is monobasic, two of its three atoms of hydrogen being unreplaceable by basic metals. The barium salt is accordingly represented by the formula $(PO^2H^2)^2Ba$; and the potassic hypophosphite is $PO^2H^2K$.

In contact with nascent hydrogen hypophosphorous acid evolves phosphuretted hydrogen. Phosphorous acid gives rise to the same product when similarly treated. Cupric hypophosphite undergoes a remarkable decomposition when a solution of the salt is allowed to stand for a few hours. A red brown powder, consisting of cuprous hydride, is deposited from the salt, together with metallic copper. The cuprous hydride dissolves with facility in hydrochloric acid, with evolutions of hydrogen, a property which metallic copper does not possess—

$$Cu^2H^2 + (HCl)^2 = Cu^2Cl^2 + H^4.$$

**135. Phosphuretted Hydrogen** ($PH^3 = 2$ vols.) is a gas analogous to ammonia, but possessing feebler basic properties. It is easily obtained by heating hydric phosphite. The gas has an unpleasant smell of rotten fish. It is easily condensed by pressure to a liquid. With an equal volume of hydriodic acid gas it combines, forming a salt, which crystallizes in beautiful cubical crystals, and is represented by the formula $PH^4I$. This salt is decomposed by water into hydriodic acid, which dissolves, and

phosphuretted hydrogen, which is given off. Pure phosphuretted hydrogen is not spontaneously inflammable, but it can easily be kindled, and burns with a bright flame.

When phosphuretted hydrogen is evolved by the action of phosphorus on aqueous potash, it contains another compound which is spontaneously inflammable. This compound can be condensed to the liquid state by cold, and is said to have the composition $PH^3$; but it requires further investigation.

**136. Phosphorous Chloride** ($PCl^3$ = 2 vols.) Clear phosphorus burns vividly, but with a pale flame, in dry chlorine; and if the product be distilled with an excess of phosphorus it constitutes a liquid of 1.45 density, and boiling without decomposition at 78°C. Phosphorous chloride fumes in the air, and decomposes water rapidly. It decomposes many oxides and hydrated oxides, in a manner similar to that in which it decomposes water, chlorine combining with hydrogen, or with any substance like hydrogen, and the phosphorus forming a phosphite ($PO^3H^3$).

**Phosphoric Chloride** ($PCl^5$ = 4 vols.) is easily obtained from phosphorus, or from the phosphorous chloride, by the action of chlorine. It is a solid crystalline compound, and appears to break up on distillation into phosphorous chloride and free chlorine, which reunite rapidly at the lower temperature of the condenser. This compound is one of the most powerful agents for the decomposition of oxides.

With a small quantity of water it decomposes into a liquid compound called chlorophosphoric acid, while hydrochloric acid is given off. The reaction is as follows:—

$$PCl^5 + H^2O = POCl^3 + (HCl)^2;$$

and chlorophosphoric acid is in its turn readily decomposed by water, forming hydric-phosphate and chloride—

$$POCl^3 + (H^2O)^3 = PO^4H^3 + (HCl)^3.$$

It is probable that the first reaction is

$$P\,O\,Cl^3 + H^2\,O = P\,O^2\,Cl + (H\,Cl)^2,$$

and that this chloride reacts on another molecule of water,

$$P\,O^2\,Cl + H^2\,O = P\,O^3\,H + (H\,Cl),$$

leaving the metaphosphoric acid to take up a molecule of water, and to become tribasic salt.

Ammonia decomposes phosphoric chloride, forming amongst other products the phosphoric chloronitride $P^3\,N^3\,Cl^6$.

Chlorophosphoric acid has a vapour density of 78.75; for its molecule $P\,O\,Cl^3$ occupies 2 volumes. In the liquid state it has a density of 1.7, and it boils at 110°C.

Sulphuretted hydrogen decomposes phosphoric chloride in the same way that water does—

$$P\,Cl^5 + H^2\,S = P\,S\,Cl^3 + (H\,Cl)^2.$$

Bromine combines with phosphorus in a similar manner to chlorine, forming phosphorous bromide ($P\,Br^3$) and phosphoric bromide ($P\,Br^5$).

Iodine has not been found to form phosphoric iodide. It forms however phosphorous iodide, which crystallizes from sulphide of carbon, and also a beautiful crystalline biniodide ($P^2\,I^4$). Both of these iodides of phosphorus decompose oxides in the same sort of way as the chlorides of phosphorus decompose them. But owing to the slight force with which iodine combines with hydrogen or bodies like hydrogen, the reactions are less violent.

**137.** There are three well-characterized sulphides of phosphorus, $P^2\,S$, $P^2\,S^3$, and $P^2\,S^5$; all of which combine with alkaline sulphides, forming sulphur salts, corresponding to the oxygen salts of hypophosphorous, phosphorous, and phosphoric acids.

Clear phosphorus and sulphur combine with such violence that considerable care should be taken in heating the two elements together. With red phosphorus the action is however much more tranquil and convenient, and the sulphides

are best made from this kind of phosphorus. Both phosphorous sulphide and phosphoric sulphide are decomposed by water, with formation of phosphorous and phosphoric acids respectively. Berzelius investigated and described a hypophosphorous subsulphide ($P^4S$).

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# CHAPTER XX.

**138. Boron** (B = 11) is reduced from boracic acid, or from boric fluoride, by sodium. Freshly prepared boron dissolves in water, but after exposure to a white heat it is insoluble. The black powder thus obtained is as infusible as lamp-black, and cannot be volatilized.

Deville and Wöhler have obtained boron in the form of crystals by depositing it from solution in melted aluminium.

Only one compound of boron with oxygen is known, viz. boracic acid ($B^2O^3$).

This acid can be prepared from commercial borax, which is a sodic diborate. The salt is dissolved in water with the aid of heat, and gradually decomposed by sulphuric acid. The necessary quantity of sulphuric acid can be estimated by the action of the liquid on blue litmus-paper. Free boracic acid imparts to the paper a dull red colour, but as soon as all the acid is expelled and a little additional sulphuric acid added to the liquid, a bright red colour immediately makes its appearance, and indicates the completion of the decomposition. On the liquid becoming cool, hydric borate ($BO^3H^3$) crystallizes out from it, and can be purified by recrystallization. The acid easily gives up its water when melted in a platinum crucible, and forms a clear glass.

Boracic acid evaporates readily in a current of steam, and is collected by condensation of steam in some volcanic districts of Tuscany. It imparts to the flame of alcohol a green colour. The acid cannot be completely precipitated from a solution by any known process, and its detection and estimation in mixtures are operations of some difficulty.

The borates are chiefly of two classes—namely, orthoborates (such as the normal trisodic borate $BO^3Na^3$), and the penta-hydro-potassic diborate ($B^2O^6H^5K$), and metaborates (such as the potassic borate $BO^2K$).

Boric nitride (BN) is formed by direct combination of boron with nitrogen at a red heat. It is a very inert substance. It is decomposed by steam at a high temperature, forming boracic acid and ammonia.

Boric chloride ($BCl^3 = 2$ vols.) is formed by passing chlorine gas through a red-hot porcelain tube containing a mixture of boracic acid and charcoal. It is a mobile liquid, boiling at 18°. In contact with water it is rapidly decomposed, forming hydrochloric acid and a borate—

$$BCl^3 + (H^2O)^3 = BO^3H^3 + (HCl)^3.$$

Boric sulphide ($B^2S^3$) can be obtained by burning boron in sulphur. It is decomposed by water.

**139. Silicon** (Si = 28) is found as silicic acid (usually called silica) in the greater number of rocks. In its physical characters silicon has some resemblance to carbon and boron. It is prepared from potassic fluosilicate by the action of sodium, and if metallic zinc be present, the silicon is obtained in the form of crystals, which are not attacked by sulphuric acid nor by aqueous hydrochloric acid. Some alloys of silicon present valuable properties, for which it seems not unlikely that they may become articles of manufacture.

Amorphous silicon decomposes hydrochloric acid gas, forming a liquid compound containing silicon, chlorine, and hydrogen. This chlorohydride of silicon boils at about 42°C,

and its vapour burns as easily as ether. It is not unlikely that it may have the composition $SiCl^3H = SiCl^2(ClH)$.

**Silica** or silicic acid ($SiO^2$) occurs pure as rock crystal. From felspar or any other silicate, however insoluble, the acid can be obtained by fusion with sodio-potassic carbonate. The fused mass is dissolved in dilute hydrochloric acid, and evaporated to dryness, with an excess of that acid. All the bases contained in the original mineral can be dissolved by hydrochloric acid from this dried mass, leaving the silica in the form of a fine white powder. When silica is first expelled from a solution of one of its salts, such as sodic silicate, in presence of much water, by hydrochloric acid, it is in the form of a hydrate soluble in water, and by placing such a mixture of silica solution and sodic chloride onto his so-called dyalyzer, Professor Graham has succeeded in diffusing out all the sodic chloride and obtaining a solution of pure silicic acid in water. Such a solution gelatinizes on standing.

The solution of silicic acid no doubt contains the tetrahydrate $SiO^4H^4$, but there is also the dihydrate $SiO^3H^2$, besides others containing still less water.

At ordinary temperatures silica is a very weak acid, but at a red heat it is capable of expelling even sulphuric acid from its salts; and this must be attributed in some measure to the fact that at these high temperatures sulphuric acid evaporates readily, whereas silica cannot be volatilized, even at the highest artificial temperatures.

The composition of the silicates presents many varieties. Some correspond to the hydric silicate $SiO^4H^4$—for instance, $SiO^4Mg^2$, in which $Mg^2$ (two atoms of magnesium) occupy the place of the four atoms of hydrogen of the acid—others, such as $SiO^3Na^2$, correspond to the lower hydrate, and there are also the following amongst other silicates—

$$Si^2O^5K^2,\quad Si^3O^7Na^2,\quad Si^4O^9Na^2.$$

Silicous oxide (Si O?) is formed by dissolving silicic chlorohydride in water at 0°. It decomposes water rapidly with evolution of hydrogen in presence of alkalies, forming a silicate.

Siliciuretted hydrogen is obtained together with hydrogen by dissolving an alloy of silicon and magnesium in hydrochloric acid. It has also been obtained with similar properties by using a piece of aluminium alloyed with silicon as the positive pole in conducting the current of a battery through a solution of sodic chloride. Hydrogen is evolved at both poles while the positive pole combines with chlorine, and a part of its materials no doubt decompose water. The compound is spontaneously inflammable in air.

**140. Silicic Chloride** ($Si\,Cl^4$ = 2 vols.) is formed by a similar process to that adopted in the preparation of boric chloride. It boils at 50°C, and its vapour is rapidly decomposed by moisture.

Silicic fluoride ($Si\,F^4$ = 2 vols.) is readily formed by the action of hydrofluoric acid on silica or any compound of silica. It is most easily prepared by heating a mixture of fine quartz sand and fluorspar in a platinum retort with fuming oil of vitriol—

$$Si\,O^2 + (Ca\,F^2)^2 + (S^2\,O^7\,H^2)^2 = Si\,F^4 + (So^4\,Ca)^2 + (So^4\,H^2)^2;$$

and collecting the gas over mercury. The fluoride is readily absorbed and decomposed by water, one-third of the silicon being deposited in the form of silica, while the other two-thirds remain in combination with fluorine and hydrogen—

$$(Si\,F^4)^3 + (H^2\,O)^2 = (Si\,F^6\,H^2)^2 + Si\,O^2.$$

## APPENDICES TO CHAPTERS XVII—XX.

### Problems.

119. What would be the vapour volume of 10 grammes of hydric sulphate ($H^2\,S\,O^4$) at 400°C?

120. What volume of the vapour of carbonic sulphide,

measured at 100°C and 760 mm., could you obtain by combining 100 grammes of carbon with sulphur?

121. What volume of oxygen is needed for the combustion of 10 grammes of carbonic sulphide? What volume of each product is formed?

122. What volume of nitric oxide is needed for the complete combustion of 10 grammes of carbonic sulphide?

123. What is the weight of a litre of hyposulphurous subchloride ($S^2Cl^2$) at 200° C?

124. What volume of hydrochloric acid would be formed if a litre of chlorosulphuric acid vapour were decomposed by water?

125. What volume of hydriodic acid would combine with one litre of phosphuretted hydrogen?

126. What volume of oxygen would be required for the complete combustion of a cubic centimeter of phosphuretted hydrogen?

127. What volume of phosphorous chloride could be obtained by combining one litre of chlorine with phosphorus?

128. 10 grammes of phosphorus are saturated with chlorine. What is the vapour volume of the product, calculated at 0°C and 760 mm.?

129. What volume of chlorine could be taken up by a litre of phosphuretted hydrogen?

130. What volume of hydrochloric acid would be obtained by replacing, by an equivalent weight of hydrogen, the boron in one litre of boric chloride (calculated at 0°C)?

131. What weight of boron is contained in a litre of boric fluoride?

132. 10 grammes of silica are converted into silicic fluoride. What is the volume of the gas?

133. 50 grammes of silicic chloride are decomposed by water. What weight of dry silica is formed?

# CHAPTER XXI.

**141. Arsenic** (As = 75; $As^4$ = 2 vols.) is a white and brittle metal, which evaporates easily when heated, but does not melt. Its vapour has a peculiar odour, which is compared to the odour of garlic. Arsenic burns with a blueish flame, forming arsenious acid ($As^2O^3$), and in moist air it undergoes gradual oxidation at the ordinary temperature. The preparation of metallic arsenic is an important test for the presence of any of its compounds, and ought to form part of the investigation in every case of suspected poisoning by arsenic.

Arsenious acid mixed with charcoal is easily reduced by the action of heat, and the metal collects on the nearest cold place in the tube in which the mixture is heated. Another very common way of obtaining metallic arsenic is by Marsh's test. The first operation is to pour the solution of arsenious acid into a mixture of metallic zinc and dilute sulphuric acid, and thus prepare hydrogen containing a volatile compound of arsenic and hydrogen. This compound is then decomposed by passing it through a glass tube heated strongly by a gas flame. A ring of metallic arsenic is thus obtained beyond the hot part of the tube. If the hydrogen containing the arseniuretted hydrogen be allowed to come out at a fine point in a glass tube and there kindled, it burns with a blueish flame, and a piece of cold porcelain held in the flame becomes marked by a brown spot of metallic arsenic. Arsenic is readily dissolved by nitric acid, or by an aqueous solution of so-called bleaching-powder. Hydrochloric acid has scarcely any action upon it. There are two compounds of arsenic with oxygen—viz. arsenious acid ($As^2O^3$) and arsenic acid ($As^2O^5$).

**142. Arsenious Acid** is commonly sold by the name of "arsenic" or white arsenic. It usually occurs as a white crystalline powder, but it can also be obtained by fusion in the form of a glassy mass, which gradually becomes white and opaque, like porcelain. The acid dissolves slowly in water, and its solution has a feebly acid reaction; and anhydrous crystals are deposited, on cooling, from a solution saturated at the boiling-point. It dissolves readily in caustic potash, and can slowly expel carbonic acid from potassic carbonate. Aqueous hydrochloric acid dissolves arsenious acid readily, but on boiling a solution in concentrated hydrochloric acid, arsenious chloride is volatilized. Aqueous arsenious acid is precipitated by an excess of lime-water, the precipitate having a composition represented by the formula $As O^3 Ca H$. A solution of argentic nitrate is scarcely affected by an aqueous solution of arsenious acid, but the addition of ammonia causes the precipitation of yellow argentic arsenite—

$$As O^3 Ag^3.$$

Sulphuretted hydrogen causes a yellow colour in a solution of arsenious acid in water, and yellow arsenious sulphide is precipitated from the mixture on the addition of hydrochloric acid; $As^2O^3 + (H^2S)^3 = As^2S^3 + (H^2O)^3$.

Metallic copper immersed in a solution of arsenious acid acidulated by hydrochloric acid reduces the metal and becomes coated with a grey film.

Zinc immersed in such a solution evolves hydrogen containing arseniuretted hydrogen.

Arsenious acid forms with ferric oxide a compound insoluble in water, and the ferric hydrate is accordingly administered as an antidote for arsenious acid.

**143. Arsenic Acid** ($As^2O^5$) is readily obtained by the action of nitric acid on arsenious acid. It is a much stronger acid than arsenious, and dissolves much more readily in water, forming an intensely acid solution. It forms the

normal hydrate $As O^4 H^3$, from which all the water can gradually be expelled by the application of heat; lower hydrates being first formed. Arsenic acid cannot be volatilized without decomposition, for when sufficiently heated it breaks up into arsenious acid and oxygen. Its solution expels carbonic acid from sodic carbonate, forming the salt $As O^4 Na^2 H (H^2 O)^{12}$, isomorphous with common hydrodisodic phosphate. There is also a sodic arseniate containing three atoms of sodium ($As O^4 Na^3 (H^2 O)^{12}$), and another containing only one atom of sodium and two of basic hydrogen ($As O^4 Na H^2 (H^2 O)$), having a strongly acid reaction.

Arsenic acid is easily distinguished from arsenious acid by the red-brown colour of the argentic arseniate $As O^4 Ag^3$. Its solution is very slowly reduced by sulphuretted hydrogen with deposition of sulphur—

$$As O^4 H^3 + H^2 S = As O^3 H^3 + S + H^2 O.$$

The arsenious acid thus formed is subsequently decomposed, forming arsenious sulphide, but the process is so extremely slow that arsenic acid is usually reduced by boiling with sulphurous acid prior to the action of sulphuretted hydrogen. Arsenic acid forms with magnesia and ammonia an important double salt, $As O^4 Mg N H^4 (H^2 O)^6$, which serves for the quantitative estimation of the acid. This salt loses none of its ammonia at the heat of the water-bath.

**144. Arseniuretted Hydrogen** ($As H^3$ = 2 vols) is readily formed together with hydrogen when arsenious acid is present in a mixture of dilute sulphuric acid and metallic zinc; $As^2 O^3 + H^{12} = (As H^3)^2 + (H^2 O)^3$. The process goes commonly by the name of Marsh's test. It is a very poisonous gas, condensible by cold. When hydrogen containing arseniuretted hydrogen is passed into a solution of argentic nitrate, a reduction of metallic silver takes place simultaneously with a formation of arsenious acid.

Arsenious chloride ($As Cl^3$ = 2 vols.) Metallic arsenic burns in chlorine gas, forming this chloride, whatever may be the proportions of the materials employed. The compound is at the ordinary temperature a heavy liquid; it boils at 132°C. It combines with water, but in presence of a large quantity of water it is decomposed into arsenious acid and hydrochloric acid. When arsenious acid or one of its salts is distilled with hydrochloric acid of 1.1 density arsenious chloride passes over with the aqueous acid, and the reaction affords an excellent means of separating arsenic from organic or other bodies which would interfere with its other reactions.

Arsenic forms a tribromide which is solid at the ordinary temperature. Also a corresponding iodide which is obtained in the form of red crystals.

**145.** Three sulphides of arsenic are known—namely, a red bisulphide ($As^2 S^2$) commonly called realgar; a yellow tersulphide (arsenious sulphide—$As^2 S^3$); and a pentasulphide (arsenic sulphide), which is also yellow.

Arsenious sulphide is readily obtained by passing sulphuretted hydrogen through a solution of arsenious acid, containing free hydrochloric acid. It is insoluble in hydrochloric acid but dissolves in ammonia sulphide, forming ammonic sulphursenite ($As S^3 (N H^4)^3$).

Free mineral acids readily decompose the solution of this salt, precipitating arsenious sulphide and liberating sulphuretted hydrogen—

$$(As S^3 (N H^4)^3)^2 + (H Cl)^6 = As^2 S^3 + (H^2 S)^3 + (N H^4 Cl)^6.$$

Arsenic sulphide dissolves readily in caustic alkalies, and it even dissolves, though less readily, in ammonia carbonate.

It evaporates unchanged when heated without access of air.

Arsenic sulphide can be obtained by passing sulphuretted hydrogen into a solution of sodic arseniate as long as any

of the gas is absorbed. The oxygen of the salt is thus replaced by sulphur—

$$As\,O^4\,Na^2\,H + (H^2\,S)^4 = As\,S^4\,Na^2\,H + (H^2\,O)^4.$$

The solution of the sulphurseniate is decomposed by hydrochloric acid.

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# CHAPTER XXII.

**146. Antimony** (Sb = 122) is a very brittle crystalline metal, having a density of 6.7. It is far less volatile than arsenic, requiring a bright red heat for its volatilization, and its vapour burns in the air with a brilliant white flame.

The metal is not attacked by hydrochloric acid. Nitric acid converts it into a white oxide insoluble in the acid.

Strong sulphuric acid dissolves it with the aid of heat evolving sulphurous acid—

$$Sb^2 + (S\,O^4\,H^2)^6 = Sb^2\,(S\,O^4)^3 + (S\,O^2)^3 + (H^2\,O)^6.$$

The metal can be obtained by the action of hydrogen at a red heat upon either antimonic oxide or the antimonic sulphide. It is commonly prepared on a large scale by putting antimonic sulphide with metallic iron—

$$Sb^2\,S^3 + Fe^3 = Sb^2 + (Fe\,S)^3.$$

Antimony combines in two proportions with oxygen, forming antimonious acid, sometimes called antimonic oxide, and antimonic acid.

**147. Antimonic Oxide** ($Sb^2\,O^3$) is obtained by decomposing antimonic chloride by water. The last portions of the hydrochloric acid are best removed by the aid of a solution of sodic carbonate. The white powder is deprived of its water by the aid of heat. At a high temperature antimonic oxide melts, and it can be volatilized with difficulty.

It is dissolved by a solution of hydropotassic tartrate, forming the well-known salt tartar emetic; and in this salt the oxide does not shew the property which belongs to the chloride—of undergoing precipitation by water.

Antimonic oxide dissolves in caustic potash. It reduces metallic silver from the argentic nitrate neutralized by ammonia.

**Antimonic Acid** ($Sb^2O^5$) is formed by the action of concentrated nitric acid on metallic antimony. It is a white powder, almost insoluble in water, and soluble with difficulty in hydrochloric acid.

When strongly heated it gives off one-fifth of its oxygen, leaving a compound of two atoms of antimony with four atoms of oxygen ($Sb^2O^4$), which may be regarded as consisting of antimonic acid combined with antimonic oxide.

Antimonic acid is remarkable for forming with soda a salt nearly insoluble in water, and quite insoluble in dilute alcohol.

**148. Antimoniuretted Hydrogen** ($Sb\,H^3$) is formed in a similar manner to arseniuretted hydrogen, and resembles that compound greatly in its properties. It is decomposed by passing through a glass tube of small diameter heated by a gas flame, and a ring of bright metallic antimony is deposited from it. The ring of antimony thus obtained can be distinguished from the ring of arsenic, obtained in a similar manner from arseniuretted hydrogen, by the lesser volatility of the antimony, and also by the circumstance that the antimonic oxide formed by heating the metal in contact with air does not (like arsenious acid) dissolve in water.

When antimoniuretted hydrogen is passed into a solution of argentic nitrate, a precipitate of argentic antimonide is formed: thus,

$$Sb\,H^3 + (N\,O^3\,Ag)^3 = Sb\,Ag^3 + (N\,O^6\,H)^3.$$

A boiling solution of tartaric acid takes up antimonic oxide

from this precipitate, no doubt with the intervention of atmospheric oxygen.

Antimony combines in two proportions with chlorine—forming a trichloride (antimonious chloride) and a pentachloride (antimonic chloride).

Antimonious Choride ($SbCl^3$ = 2 vols.) is most readily prepared by dissolving lumps of antimonic sulphide in strong hydrochloric acid with the aid of heat—

$$Sb^2S^3 + (HCl)^6 = (SbCl^3)^2 + (H^2S)^3.$$

The solution thus obtained is evaporated to dryness (some chloride of antimony escaping during the process), and the antimonic chloride is purified by distillation. In this manner it is obtained in the form of a white crystalline mass.

Water decomposes the antimonious chloride, forming hydrochloric acid, and a basic chloride; and the hydrochloric acid formed by the decomposition of one part of the salt dissolves some of the chloride. When a saturated solution of antimonious chloride in concentrated hydrochloric acid is diluted with water, some of the antimony is precipitated as a basic salt, the remainder being held in solution by the more dilute hydrochloric acid.

Antimonic chloride ($SbCl^5$) is formed by passing dry chlorine into a vessel containing the trichloride. It is a heavy yellow liquid, and emits dense fumes in contact with moist air. Antimonic chloride is decomposed by heat, chlorine gas making its escape in abundance, and carrying some of the chloride with it.

**149.** Antimonic sulphide ($Sb^2S^5$) is formed by the action of sulphuretted hydrogen on solutions of the oxide, containing a moderate quantity of the mineral acid.

It is an orange-coloured precipitate, but after fusion it is much darker in colour, and the black native sulphide is the most abundant ore of antimony.

Antimonic sulphide dissolves readily in ammonia sulphide,

*but*, unlike arsenious sulphide, it does not dissolve in ammonia carbonate (carbonate of ammonia).

Antimonic persulphide ($Sb^2S^5$) is very similar to the sulphide in its appearance and properties. It forms crystallizable salts with sulphur bases, such as the sodic sulphantimoniate $Sb\,S^4Na^3(H^2O)^9$.

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# CHAPTER XXIII.

**150. Tin** (Sn = 118) is prepared chiefly from its binoxide called tinstone, from which it is easily reduced by coal. It melts at 228°C. Although crystalline in its structure, a mass of metallic tin cannot, like antimony, be reduced to powder in a mortar. The effect of hammering it is to flatten and extend the mass. Tin can even be rolled into thin foil or drawn into wire. Although it melts at a low temperature, it cannot be volatilized without great difficulty. When kept in the fluid state in contact with air, it gradually absorbs oxygen, forming the binoxide $SnO^2$.

Hydrochloric acid dissolves tin with the aid of heat, forming stannous chloride—

$$(HCl)^2 + Sn = SnCl^2 + H^2.$$

Nitric acid acts upon tin in the same sort of way as upon antimony, converting it into a white oxide insoluble in the acid.

Tin forms two definite oxides—the stannous oxide SnO, which is a strong base, and the stannic oxide $SnO^2$, commonly called stannic acid, which has feebler basic properties, and willingly acts the part of an acid.

Stannic acid is remarkable for the different properties which it manifests according to the manner in which it is

prepared. When formed by oxidation of tin by nitric acid it is insoluble in hydrochloric acid, but when prepared by the precipitation of a solution of stannic chloride by a carbonate it is readily soluble in hydrochloric acid. The soluble kind becomes insoluble by heat, and on the other hand, the insoluble variety can be rendered soluble by fusion with caustic potash.

Tartaric acid does not dissolve the stannic oxide formed by nitric acid, and affords in this manner a convenient distinction between tin and antimony.

**151. Stannous Chloride** ($Sn\ Cl^2$) is usually prepared in combination with water by dissolving the metal in hydrochloric acid. The crystals which are deposited from the solution after concentration contain two molecules of water of crystallization ($Sn\ Cl^2\ (H^2\ O)^2$). They are decomposed by water in the same sort of way as antimonic chloride, though to a lesser degree. The water cannot be expelled from these crystals by heat without carrying away hydrochloric acid. Stannous chloride absorbs oxygen readily, and is a powerful reducing agent. When mixed with a solution of auric chloride it causes the appearance of a deep brown colour; and if sufficient quantity of the materials is used, a precipitate of Cassian purple is formed.

Tin is not precipitated by iron from a solution of its chloride.

**152. Stannic Chloride** ($Sn\ Cl^4 = .2$ vols.) This volatile liquid was formerly known by the name of fuming spirit of Libavius. It is most easily prepared by distilling granulated tin with about four times its weight of mercuric chloride, care being taken to exclude moisture. It combines with a small quantity of water, forming crystals of a hydrate. A large quantity of water decomposes its solution slightly into hydrochloric acid, which dissolves, and gelatinous flakes of stannic hydrate.

The rare metal titanium has in its compounds considerable analogy with tin.

Tungsten, vanadium, and molybdenum constitute a natural family of metals, and the compounds of the first of them are already coming into use.

**153. Tungsten** ($W = 184$). The metal can be reduced by charcoal or hydrogen from one of its oxides, at a high temperature. It is very difficult of fusion; density 17.6.

Tungsten forms a binoxide, and a trioxide ($WO^3$) called tungstic acid.

Tungstic acid is insoluble in water and in hydrochloric acid. Its normal soda salt ($WO^4Na^2(H^2O)^2$) is prepared for impregnating cambric, and thereby rendering it uninflammable. Nascent hydrogen gradually desoxidizes tungstic acid, forming tungstic binoxide. But by carefully regulating the action it is easy to arrest the reduction half way, leaving a deep indigo-blue oxide.

Tungsten forms a bisulphide, and a trisulphide which combines with the alkaline sulphides, forming soluble sulphur salts.

Molybdic acid is chiefly interesting from the fact of its forming, together with phosphoric acid, very insoluble compounds with ammonia, or with organic bases analogous to ammonia.

**154. Gold** ($Au = 196.5$) is classed among the noble metals in virtue of its having no tendency to rust, and because most of its compounds decompose spontaneously at a high temperature. It is one of the heaviest of metals, its density varying from 19.2 to 19.4. It melts at about 1100°C. It is a very soft metal, and can be hammered out to a leaf so thin as to be transparent, allowing green rays of light to pass through it.

Gold is not dissolved by nitric, hydrochloric, or sulphuric acid, even on boiling. Its commonest solvent is a mixture

of strong hydrochloric and nitric acids, called aqua regia. The yellow solution obtained by aqua regia consists of auric trichloride. The metal is precipitated from this solution completely, in the form of a soft brown powder, by ferrous sulphate—

$$(Fe\,S\,O^4)^3 + Au\,Cl^3 = Fe\,Cl^3 + Fe^2\,(S\,O^4)^3 + Au.$$

It can also be reduced by oxalic acid.

At the melting-point of tin, auric chloride loses two atoms of chlorine, being reduced to monochloride. The auric oxide, corresponding to the trichloride, is frequently called auric acid. In the free state its composition is represented by the formula $Au^2 \cdot O^3$. Potassic aurate ($Au\,O^2\,K\,(H^2\,O)^3$) is a crystallizable salt.

Auric chloride might with equal right be called chlorauric acid, for it combines with potassic chloride, sodic chloride, &c., forming crystallizable salts: e.g., $Au\,Cl^4\,Na\,(H^2\,O)^2$.

Sulphuretted hydrogen precipitates gold from its acid solutions as a dark brown sulphide.

**155. Platinum** (Pt = 197; density 21.5) is another noble metal. In compact masses it is white, but it can be obtained by precipitation in the form of a black powder like lamp-black. The metal requires for its fusion the temperature of a flame fed with oxygen. Platinum possesses the valuable property of uniting together when two masses of it are pressed or hammered together at a high temperature. The operation of uniting two or more masses of metal into one in this manner is called 'welding.'

The process of working platinum was devised by Dr. Wollaston. The ore, which consists of white metallic particles, containing platinum combined with some other metals, is purified by boiling with nitric acid, and then with hydrochloric acid. It is then warmed with strong hydrochloric acid, with occasional additions of nitric acid. The solution containing platinic chloride is diluted, and precipitated by a

solution of ammonia chloride. The precipitate is a yellow double salt, consisting of platinic chloride combined with ammonic chloride ($PtCl^6(NH^4)^2$). This ammonia platinic chloride is collected and heated to redness, everything but platinum going off, and the platinum being left in a spongy form. This spongy platinum is heated, and compressed and hammered until it is brought down to a coherent mass of 21.5 density. A new plan has been lately brought into operation by Deville and Debray, whereby liquid metallic lead is made to dissolve out the platinum from its ore, whilst the impurities are left undissolved. The lead is subsequently burnt away from the alloy of lead and platinum, and the platinum is finally melted in a crucible of lime by a flame fed with oxygen.

Platinum is one of the most tenacious of metals, and is valuable as a material for the manufacture of vessels in which strong acids or fluorides have to be heated. It is oxidized by fusion with potash or soda in contact with air. It also combines readily with metals and phosphorus at a high temperature. The metal forms two oxides—viz. platinous oxide (PtO) and platinic oxide ($PtO^2$), both of which are bases; but the platinic oxide has almost equal claims to be classed among acids, as it combines with strong bases.

Both oxides give off all their oxygen at a high temperature. There are two sulphides corresponding in composition to the two oxides. The platinic sulphide dissolves somewhat in alkaline sulphides.

**156.** The ordinary solution of platinum is a tetrachloride, or rather a compound of the tetrachloride with hydrochloric acid ($PtCl^6H^2$).

When its solution is evaporated to dryness and carefully heated to about 230°C, it gives off hydrochloric acid and half its remaining chlorine, leaving platinous chloride ($PtCl^2$), a dark green powder insoluble in water. This platinous

chloride is decomposed in its turn by still stronger heat. Solutions of platinum are not, like those of gold, reduced by ferrous sulphate, nor by oxalic acid. Formic acid reduces platinum with the aid of heat when present in a neutral solution.

The action of ammonia on platinous chloride gives rise to the formation of bases, which consist of ammonia in which a part of the hydrogen is replaced by platinum. In illustration of these remarkable bodies may be mentioned the compound $PtCl^2N^4H^{12}$, which is formed by dissolving platinous chloride in ammonia and crystallizing the solution. It is considered to be a compound of hydrochloric acid with a kind of ammonia, consisting of $N^4H^{10}Pt$. In this base one atom of platinum holds the place of two atoms of hydrogen in the group $N^4H^{12}$. By heating the salt ammonia can be easily expelled, and the compound $PtCl^2N^2H^6$ is obtained. The rational formula by which this body is explained is $Pt\left\{\begin{matrix}NH^3\\NH^3\end{matrix}\right\}Cl^2$, representing it as the chloride of an ammonium of the composition $Pt\left\{\begin{matrix}NH^3\\NH^3.\end{matrix}\right.$

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# CHAPTER XXIV.

**157. Silver** (Ag = 108 ; sp. gr. = 10.5 ; melting-point, 1023°). This most beautiful metal is sometimes found in the pure state as so-called native silver. It also occurs with other metals, in combination with sulphur, and among ores of this kind galena is the most plentiful. This mineral consists mainly of plumbic sulphide, but the metallic lead prepared from nearly all samples of it contains a small

*quantity* of silver. Although the quantity of silver frequently amounts only to a few ounces in the ton of lead, it is profitably extracted by Pattinson's admirable process. This process consists in melting the argentiferous lead in large iron pots, and allowing the molten mass to cool gradually. Crystals soon make their appearance in the mass, and these are removed by iron strainers as fast as they appear, until the greater part of the contents of the pot have been removed in the form of crystals. These crystals are melted in a second pot, and separated by a second crystallization while they are cooling, and the process is repeated until at last crystals are obtained containing only about half an ounce of silver in the ton, while the greater part of the silver is collected in those portions of lead which were left in the pots after the removal of the crystals of lead. The final purification of the silver is by so-called cupellation, which is a process of burning away the metallic lead in a shallow vessel called a cupel, heated by flames which are made to play over its surface. The silver is left free from lead, and copper, if present in small quantity, is removed by the plumbic oxide.

Silver possesses the remarkable property of absorbing oxygen from the air while it is liquid, and giving the gas off again while it is solidifying. When a mass of molten silver is allowed to cool, the film of solid metal which is formed upon its surface is raised and burst in several places by the escaping oxygen. This phenomenon is called spitting, and a loss of silver is very liable to occur during cooling.

Standard silver is an alloy containing 7.5 per cent. of copper to 92.5 of silver.

**158.** Silver dissolves readily in nitric acid, and with the aid of heat in strong sulphuric acid. Hydrochloric acid has scarcely any action upon it.

It forms with oxygen the strong base argentic oxide $Ag^2O$ and the neutral peroxide $Ag^2O^2$. There is also

some reason to believe in the existence of a suboxide $Ag^4O$. These oxides are completely decomposed by heat.

Argentic oxide can be obtained by cautiously heating argentic nitrate. Caustic potash added to a solution of the nitrate precipitates the hydrate Ag H O. Ammonia produces a similar effect, but an excess of ammonia readily dissolves the hydrate.

**Argentic Oxide** is remarkable among bases for forming anhydrous salts, and a silver salt is the best one to prepare and analyze, whenever the molecular weight of an acid has to be determined with the utmost trustworthiness. By the action of light, silver is readily reduced to the metallic state from its salts, if any oxidizable matter be present. Formic acid reduces it rapidly with the aid of heat, in neutral solutions, in the form of a light grey powder. Sulphurous acid acts in a similar manner.

Argentic nitrate ($NO^3Ag$), or "lunar caustic," is one of the most important salts of the metal. It crystallizes in plates which contain no water. The salt dissolves in about its own weight of water at 15°C. When heated it melts to a clear liquid, and does not decompose until heated to a higher temperature.

Oxalic acid forms with oxide of silver a white salt, insoluble in water but soluble in nitric acid.

Carbonic acid forms with argentic oxide a yellowish salt, insoluble in water but readily dissolved by nitric acid. Its composition is represented by the formula $CO^3Ag^2$.

Argentic cyanide (C N Ag) is obtained as an amorphous white precipitate, when prussic acid is added to a solution of argentic nitrate. It is not dissolved by nitric acid in the cold, but dissolves on boiling. Ammonia dissolves argentic cyanide. It is decomposed by heat.

**159. Argentic Chloride** (Ag Cl) is a salt which is quite insoluble in water. It is thrown down in the form of a

curdy white precipitate, devoid of all crystalline structure, when argentic nitrate is mixed with a soluble chloride, such as hydrochloric acid or sodic chloride—

$$N O^3Ag + Cl Na = Cl Ag + N O^3Na.$$

It is not dissolved by nitric acid even on boiling, but is readily dissolved by ammonia. When heated strongly by itself argentic chloride melts, and on cooling has the appearance of horn, from which circumstance it has been named horn-silver. Its chlorine is carried away by volatile hydrocarbons, at a high temperature; and metallic silver is easily obtained from the chloride by melting it with sodic-carbonate, when oxygen and carbonic acid are given off.

When argentic chloride is moistened with dilute sulphuric acid, and a piece of metallic zinc is immersed in the acid and made to touch the chloride, a gradual transfer of the chlorine from the silver to the zinc takes place, first at the spot at which the zinc touches the chloride, and from that onwards through the whole mass—

$$(Ag Cl)^2 + Zn = Ag^2 + Zn Cl^2.$$

Argentic chloride is readily dissolved by sodic hyposulphite; also by potassic cyanide.

A saturated solution of sodic chloride dissolves an appreciable quantity of argentic chloride, but the whole of the argentic chloride is precipitated when the solution is sufficiently diluted.

Argentic chloride turns dark when exposed to sunshine, the change of colour being accompanied by a loss of chlorine.

Argentic bromide is a salt much like the chloride. It is, however, less soluble in ammonia than the chloride, as can be seen by adding a solution of potassic bromide to ammonia saturated by argentic chloride.

Argentic iodide is a yellow salt, distinguishable from the chloride and bromide by being insoluble in ammonia. It

can be formed from a mixture of potassic chloride and iodide by adding argentic nitrate in quantity not sufficient to precipitate all the iodine in the solution.

**160. Argentic Sulphide** ($Ag^2S$) is a black compound which occurs in the mineral kingdom crystallized in octohedra similar to those formed by cuprous sulphide ($Cu^2S$). It is precipitated by the addition of sulphuretted hydrogen or ammonia sulphide to a solution containing silver, and it does not dissolve in an excess of ammonia sulphide. Nitric acid oxidizes the silver sulphide, and dissolves it.

Argentic sulphate ($SO^4Ag^2$) is a salt which dissolves very sparingly in water, and crystallizes in a similar form to anhydrous sodic sulphate ($SO^4na^2$).

Argentic sulphite ($Ag^2SO^3$) is obtained as a white precipitate by adding sulphurous acid to argentic nitrate. It is not easily soluble in nitric acid.

Boracic acid forms a white silver salt, but like other borates this salt is dissolved by neutral saline solutions.

Phosphoric acid forms a bright yellow silver salt, containing three atoms of silver in its molecule. The reaction between hydro-di-sodic phosphate and argentic nitrate consists in an interchange between three atoms of silver on the one hand, and two of sodium plus one of hydrogen on the other hand—

$$PO^4Na^2H + (NO^3Ag)^3 = PO^4Ag^3 + (NO^3Na)^2 + NO^3H.$$

The argentic phosphate dissolves readily in nitric acid, or in ammonia.

# CHAPTER XXV.

**161. Mercury** (Hg = 200; density 13.5; Hg = 2 vols.; vapour density 100). This metal is sometimes found native in the form of globules dispersed through the rocks, but more frequently as cinnabar, which is mercuric sulphide. Its extraction is a very simple process. A mixture of cinnabar with quick-lime is distilled in a cast-iron retort, and the vapour of mercury which passes off from the mixture is led into a receiver containing water.

Commercial mercury frequently contains lead, or some other foreign metal dissolved in it; and the presence of such impurity can, if considerable, be discovered by pouring a few drops of the mercury onto a dry plate, and then inclining the plate so as to make the metal run about on it. Pure mercury leaves no mark on the plate, but a thin metallic streak (called a tail) is left by impure mercury. Mercury freezes at $-39.5°$; it boils at 357°. In colour it approaches nearly to silver, and in one class of its compounds it possesses some analogy with that metal. It is, however, a diatomic metal, and has a great tendency to form basic salts, as well as double salts, in which two different atoms of acid radical are combined with one atom of the metal. Hydrochloric acid has no action upon it. Strong sulphuric acid is decomposed by it with the aid of heat, forming mercuric sulphate and sulphurous acid.

Nitric acid dissolves the metal readily; but the compound formed by the action of a small quantity of nitric acid, insufficient to dissolve all the mercury, is mercurous nitrate

($Hg^2(NO^3)^2$), whereas the action of an excess of nitric acid forms mercuric nitrate ($Hg(NO^3)^2$). Mercury forms two compounds with oxygen, both of which are bases.

**162.** Mercurous oxide ($Hg^2O$) can be obtained by the action of potash on calomel or mercurous nitrate. It is a dark grey powder, but is decomposed readily by heat into free metallic mercury, and red mercuric oxide—

$$Hg^2O = Hg + HgO.$$

The oxygen in mercurous oxide,

$$Hg^2O + (HCl)^2 = Hg^2Cl^2 + H^2O,$$

can be replaced by two atoms of chlorine, or of bromine, or iodine; or by two atoms of the monatomic salt radical $NO^3$. In like manner it can be replaced by one atom of sulphur. These compounds are called subsalts of mercury, or mercurous salts.

**Red Oxide** of mercury, or mercuric oxide, is formed by prolonged boiling of the metal in contact with air; but a far more convenient way of preparing it is to heat mercuric nitrate slowly and cautiously as long as any red fumes come off from it. Too strong a heat would decompose the oxide, driving off oxygen and metallic mercury.

When potash is added to a solution of mercuric nitrate or chloride, the oxide is thrown down in the form of a bright yellow powder, owing to the finely-divided state in which its particles are then precipitated, and the common red oxide becomes yellower the more finely it is powdered.

Both oxides of mercury are remarkable for the facility with which they form basic salts.

Mercurous nitrate is best prepared by warming nitric acid, diluted with four times its volume of water, with an excess of metallic mercury, pouring the solution off from the residual metal, and crystallizing it after the addition of some more nitric acid. The crystals contain

$$(HgNO^3)^2(H^2O)^3.$$

By the action of water this salt is decomposed, forming a yellow double salt—

$$(Hg\,N\,O^3)^2\,(H^2\,O)^3 + (H^2\,O)^n = Hg^2\,N\,O^3\,H\,O + \\ + N\,O^3\,H + (H^2\,O)^{n+2}.$$

There is also a soluble mercurous hydro-trinitrate, having a composition represented by the formula $Hg^4\,(N\,O^3)^3\,H\,O$.

Mercuric nitrate ($Hg\,(N\,O^3)^2$) is obtained by boiling the metal with nitric acid until a sample of the solution, diluted with water, gives no precipitate with a soluble chloride. The solution when freed by evaporation from its excess of acid, deposits, on cooling, crystals of the hydro-nitrate $Hg\,N\,O^3\,H\,O$, and these in their turn are readily decomposed by water, with formation of a more basic salt of yellow colour.

Mercuric cyanide ($Hg\,(C\,N)^2$) is a salt of considerable stability, for it is not decomposed by a solution of potash. Prussic acid dissolves mercuric oxide readily, and forms, with an excess of the oxide, a soluble basic cyanide which has an alkaline reaction to test-paper. Prussic acid, added to a solution of mercurous nitrate, forms mercuric cyanide, and precipitates metallic mercury—

$$(C\,N\,H)^2 + (Hg\,N\,O^3)^2 = Hg\,(C\,N)^2 + Hg + (N\,O^3\,H)^2.$$

**163. Mercurous Chloride** ($Hg^2\,Cl^2 = 4$ vols.; vapour density = 117.75), generally called calomel, is obtained by precipitating mercurous nitrate by a solution of common salt—

$$Hg^2\,(N\,O^3)^2 + (Na\,Cl)^2 = Hg^2\,Cl^2 + (Na\,N\,O^3)^2.$$

It is also formed by the action of reducing agents, such as sulphurous acid, on a mixture of common salt with a soluble mercuric salt—

$$H^2\,O\,(Hg\,(N\,O^3)^2)^2 + S\,O^3\,H^2 + (Cl\,Na)^2 = Hg^2\,Cl^2 + \\ + S\,O^4\,Na^2 + (N\,O^3\,H)^4.$$

It is easily prepared on a large scale by heating together

a mixture of mercuric sulphate, metallic mercury, and common salt—

$$Hg\,S\,O^4 + Hg + (Na\,Cl)^2 = Hg^2\,Cl^2 + S\,O^4\,Na^2.$$

Calomel is quite insoluble in water, but it sometimes contains corrosive sublimate, which can easily be detected by its solubility in water. Calomel is decomposed by boiling with hydrochloric acid into mercuric chloride and free metallic mercury. The same action is exerted, though more slowly, by soluble chlorides.

It does not dissolve in dilute nitric acid in the cold.

Ammonia blackens it, dissolving out half of its chlorine, and replacing the chlorine so removed by amidogen ($N\,H^2$)—

$$Hg^2\,Cl^2 + (N\,H^3)^2 = Hg^2\,Cl\,N\,H^2 + N\,H^4\,Cl.$$

**164. Mercuric Chloride,** or corrosive sublimate ($HgCl^2$ = 2 vols.; spec. grav. of vapour 135.5), can be obtained by dissolving mercuric oxide in hydrochloric acid, or by subliming a mixture of salt and mercuric sulphate—

$$(Cl\,Na)^2 + Hg\,S\,O^4 = Cl^2\,Hg + S\,O^4\,Na^2.$$

Corrosive sublimate dissolves in water, and still more readily in alcohol.

Sulphuretted hydrogen, passed gradually into its solution, gives at first a brown precipitate, which becomes white by agitation with an excess of the chloride. The white precipitate is a mercuric sulphochloride. An excess of sulphuretted hydrogen converts this white precipitate into black sulphide.

Ammonia added in excess to a solution of mercuric chloride forms a white precipitate, which is used in medicine by the name of 'white precipitate.' The action is perfectly similar to that between calomel and ammonia, viz. an interchange of $N\,H^2$ and Cl—

$$Hg\,Cl^2 + (N\,H^3)^2 = Hg\,N\,H^2\,Cl + N\,H^4\,Cl.$$

This white precipitate is soluble in nitric or in hydrochloric acid.

Potash precipitates yellow mercuric oxide from a solution of chloride, and potassic carbonate forms a somewhat darker precipitate, containing scarcely any carbonic acid.

Corrosive sublimate is precipitated by albumen, and this substance is accordingly administered as an antidote in all cases of suspected poisoning by the sublimate.

A solution of corrosive sublimate is decomposed by metallic copper, the mercury being deposited upon the surface of the metal in the form of a grey coating, which shews the metallic lustre of mercury after rubbing—

$$Hg\,Cl^2 + Cu = Hg + Cu\,Cl^2.$$

Mercurous iodide is an olive-green precipitate which is readily decomposed by an excess of potassic iodide, into red mercuric iodide, which dissolves, and grey metallic mercury, which remains undissolved.

The mercuric iodide is precipitated in the form of a brilliant scarlet powder, when mercuric chloride is mixed with potassic iodide. It fuses when strongly heated, and then evaporates, but the crystals which are formed by the condensation of its vapour are of a bright yellow colour. When kept at the common atmospheric temperature these yellow crystals rapidly turn scarlet again.

**165. Mercuric Sulphide**, or cinnabar (Hg S), is the chief ore of mercury. It is prepared of a deep red colour by combining metallic mercury with sulphur dissolved in potassic sulphide. When formed by the action of an excess of sulphuretted hydrogen on a solution of mercuric salt it is black.

The black sulphide can be sublimed in a closed vessel, and it thereby acquires a red colour.

Mercuric sulphide is not attacked even by boiling nitric acid, but it is dissolved by aqua regia.

Mercurous sulphide is a black powder formed by the action of sulphuretted hydrogen on a mercurous salt.

Mercuric sulphate is a white crystalline salt, which is easily

prepared by dissolving the metal in hot and concentrated sulphuric acid. The salt is decomposed by water, leaving a bright yellow basic salt (called mineral turpeth) undissolved, while sulphuric acid is formed and dissolves some of the sulphate. The decomposition is represented by the equation

$$(S O^4 Hg)^3 + (H^2 O)^2 = S O^6 Hg^3 + (S O^4 H^2)^2.$$

Phosphoric acid forms with mercurous oxide a yellowish salt insoluble in water; and with mercuric oxide it forms a compound of very similar appearance, which is dissolved by sodic chloride.

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## CHAPTER XXVI.

**166. Lead** (Pb = 207; sp. gr. = 11.4). This metal is remarkable for its softness, which is so great, that lead can be indented by the nail. It is made on a large scale by roasting galena, and then heating the residual ore with the plumbic oxide and sulphate which have been formed. In the first stage of the operation sulphurous acid is evolved while a mixture of plumbic oxide and plumbic sulphate are formed—

$$Pb S + O^3 = Pb O + S O^2; \quad Pb S + O^4 = Pb S O^4.$$

In the second stage these products give up their oxygen and sulphur by heating with galena—

$$(Pb O)^2 + Pb S = Pb^3 + S O^2;$$
$$Pb S O^4 + Pb S = Pb^2 + (S O^2)^2.$$

Lead evaporates at a white heat, and its oxide is carried away easily by the gases in the flue during the reduction of the metal. The flues are in some lead-works constructed of great length, so as to collect this oxide as completely as possible.

Antimony and tin, when present in metallic lead, can in great part be removed by refining, which is a process of oxidizing the impurities in the lead by keeping the metal in a liquid state exposed to the action of air. Lead is oxidized at the same time, but less rapidly than those metals.

For laboratory purposes pure metallic lead is most easily obtained by fusing some plumbic acetate with crude potassic bitartrate.

Lead melts at about 325°. It expands greatly when heated, and does not on cooling always return to its original dimensions.

It is oxidized by moist air, and pure water containing oxygen dissolves plumbic oxide when placed in contact with the metal. For this reason leaden cisterns ought never to be used for collecting rain-water for domestic purposes.

**167.** Lead forms two definite oxides—the basic protoxide Pb O, called plumbic oxide, commercially called litharge, and the neutral binoxide Pb $O^2$.

**Plumbic Oxide** is best obtained in a pure state by boiling finely-powdered litharge with a solution of plumbic acetate. A basic salt is thus formed which has an alkaline reaction to litmus-paper, and which readily absorbs free carbonic acid. The liquid should be filtered and carbonic acid passed through it. A white precipitate of plumbic hydro-carbonate ($Pb^3 (C O^3)^2 (H O)^2$) is formed. This precipitate can be collected on a filter, and the plumbic acetate which is reproduced can serve to make more hydro-carbonate. When a sufficient quantity of this salt has been thus prepared it is decomposed by cautious heating in a porcelain crucible, care being taken to expel all the carbonic acid and water, without melting the mass. A yellowish white oxide is thus obtained.

Plumbic oxide melts readily at a low red heat, and dissolves glass and earthenware, readily forming fusible plumbic silicates.

Plumbic oxide is pre-eminent for its tendency to form basic salts. Thus it forms two basic hydrates,

$$Pb\,O\,Pb\,(H\,O)^2 \text{ and } (Pb\,O)^2\,Pb\,(H\,O)^2,$$

but the normal hydrate $Pb\,O^2\,H^2$ is not known.

It is dissolved readily by caustic potash, but very slightly by ammonia.

When plumbic oxide is cautiously heated in contact with air, it gradually absorbs oxygen and turns red. It is in this manner that red lead is prepared. The composition of red lead varies considerably between different samples, but they may all be considered as compounds of plumbic oxide with binoxide. The formula $Pb^3\,O^4$ represents an average composition. Nitric acid decomposes red lead, dissolving out plumbic oxide from it, and leaving brown binoxide undissolved—

$$Pb^3\,O^4 + (N\,O^3\,H)^4 = (Pb\,(N\,O^3)^2)^2 + Pb\,O^2 + (H^2\,O)^2.$$

Plumbic binoxide is decomposed by strong heat, with evolution of oxygen. When heated with strong sulphuric acid it forms plumbic sulphate, with evolution of oxygen. Hydrochloric acid decomposes it with the aid of heat, forming plumbic chloride and evolving chlorine—

$$Pb\,O^2 + (H\,Cl)^4 = Pb\,Cl^2 + Cl^2 + (H^2\,O)^2.$$

It absorbs sulphurous acid readily, forming plumbic sulphate.

**168.** Plumbic nitrate ($Pb\,N^2\,O^6$ or $Pb\,(N\,O^3)^2$) is a salt which crystallizes with facility from water. It has an acid reaction to test-paper. Its hot solution dissolves plumbic hydro-carbonate with effervescence, forming plumbic hydro-nitrate ($Pb\,N\,O^3\,H\,O$).

Plumbic carbonate ($Pb\,C\,O^3$) is found native, and is called by mineralogists lead spar. It is formed in the cold by double decomposition between sodic carbonate and plumbic acetate. Two hydro-carbonates are also known. White lead, or ceruce, consists usually of one of these com-

*pounds.* It is made by exposing gratings of metallic lead to the simultaneous action of vinegar, air, and carbonic acid. Plumbic acetate is formed, and this takes up more plumbic oxide, forming the hydro-acetate, from which carbonic acid removes the hydrate, while the normal acetate thus reproduced dissolves more oxide for a second portion of carbonic acid to act upon. In this manner a continuous circle of decompositions takes place, and is allowed to continue until a thick crust of ceruce is formed over the surface of the lead, and the further action is retarded. This crust is then removed and ground up for use as white lead.

Plumbic oxalate ($C^2O^4Pb$) is one of the most insoluble of lead salts in water, and when lead has to be precipitated from a solution, oxalic acid is one of the best re-agents. The oxalate dissolves in nitric or hydrochloric acid.

Plumbic chloride ($PbCl^2$) is a salt which dissolves but slightly in cold water. It is obtained in the form of needle-shaped crystals by slowly cooling a solution saturated at a high temperature. It fuses at a moderate heat, and has the appearance of a horny mass after cooling.

Several basic plumbic chlorides are known. The compound $Pb^2OCl^2$ is prepared by Mr. Bell, of Newcastle, for use as a white paint. $Pb^3O^2Cl^2$ is found in the mineral kingdom, and known by the name of Mendipite. $Pb^4O^3Cl^2$ is obtained by heating the precipitate formed by ammonia in a solution of plumbic chloride. A still more basic compound is used as a yellow paint and called Cassel yellow.

Plumbic iodide crystallizes from water in beautiful yellow scales.

**169. Plumbic Sulphide,** or galena (PbS), is the chief ore of lead. Sulphuretted hydrogen precipitates this black sulphide even from the most dilute solutions of plumbic salts, and is the most delicate re-agent for detecting lead. Strong hydrochloric acid dissolves the sulphide, with evolution of

sulphuretted hydrogen, but a small quantity of free hydrochloric acid does not prevent the precipitation of a solution of lead by sulphuretted hydrogen.

Dilute nitric acid dissolves out lead, leaving the sulphur; and strong nitric acid oxidizes both constituents, forming plumbic sulphate.

Plumbic sulphate ($Pb\,S\,O^4$) is a white salt, perfectly insoluble in water, but soluble in acids, in potash, and in many neutral salts, more especially in ammonia acetate or tartrate.

Plumbic sulphite ($Pb\,S\,O^3$) is very much like the sulphate in its properties.

Phosphoric acid forms a white normal salt with oxide of lead ($(PO^4)^2Pb^3$), soluble in nitric or hydrochloric acid. There is also a double salt called pyromorphite, consisting of

$$(P\,O^4)^3\,Cl\,Pb^4.$$

**170. Bismuth** (Bi = 210; sp. gr. = 9.8; melting-point, 266). This metal usually occurs native. It is exceedingly brittle, and its fracture exhibits bright crystalline surfaces of a reddish-white colour. It is easily oxidized by nitric acid, forming an oxide corresponding in constitution to antimonic oxide. Bismuthic oxide ($Bi^2\,O^3$) dissolves in nitric, hydrochloric, or sulphuric acid, but the solutions thus obtained are decomposed by the addition of water, with precipitation of an oxy salt—

$$(Bi\,Cl^3)^3 + (H^2\,O)^4 = Bi^3\,O^2\,Cl^3\,(H\,O)^2 + (H\,Cl)^6.$$

Bismuthic oxide can be prepared by heating metallic bismuth in contact with the air, or by heating the precipitate formed by potash in a solution of a salt of bismuth. It is not soluble in potash or ammonia. Its salts are remarkable for the facility with which they exchange a part of their acid for water or oxygen, forming oxy salts and double salts. Thus bismuthic chloride gives a white precipitate, which after heating consists of bismuthic oxychloride. The nitrate gives a precipitate of the composition $Bi\,N\,O^3\,(H\,O)^2$.

The normal bismuthic nitrate $Bi(NO^3)^3(H^2O)^5$ is a crystallizable salt which dissolves in dilute nitric acid. It gives off part of its nitric acid below 100°.

Bismuthic chloride ($BiCl^3$) can be distilled, and has considerable resemblance to antimonic chloride.

Bismuth forms a compound corresponding to antimonic acid. It is formed by passing chlorine through potash in which bismuth oxide is suspended.

In the anhydrous state bismuthic acid is represented by the formula $Bi^2O^5$. It forms a hydrate of the composition $BiO^3H$.

Bismuthic sulphide ($Bi^2S^3$) is a black compound, obtained by the action of sulphuretted hydrogen on acid solutions of the oxide.

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# CHAPTER XXVII.

**171. Copper** (Cu = 63.5; sp. gr. 8.9). This important metal is occasionally found native. Its chief ore is copper pyrites ($S^2CuFe$), which frequently occurs with iron pyrites.

The smelting of copper from pyrites is effected by a considerable number of operations.

A process of roasting, followed by fusion, serves to prepare a crude cuprous sulphide (called coarse metal), while the greater part of the iron is oxidised and dissolved in the slag. This coarse metal is granulated by letting it run in the molten state into water, and is then subjected to further oxidation by a process of 'roasting.' The mixture of oxides and sulphides of copper and iron thus obtained is melted

together, and the cuprous sulphide which melts out of it is finally reduced to the metallic state by fusion in a reverberatory furnace, with limited supply of air. The upper portions are fully oxidised, forming sulphurous acid and cupric oxide; but this oxide gives off its oxygen to the remaining sulphide, forming sulphurous acid and metallic copper —

$$(Cu\,O)^2 + Cu^2S = Cu^4 + S\,O^2.$$

When copper is melted in contact with air it rapidly becomes converted into black oxide, and the liquid copper dissolves a portion of cuprous oxide, and becomes thereby brittle. This impurity is removed by stirring the liquid metal with a wooden pole, the charcoal and combustible gases from which reduce the cuprous oxide to the metallic state. This operation is called poling.

Copper is sometimes obtained by the so-called process of cementation, which is a precipitation of copper from a dilute solution of cupric sulphate, by the action of metallic iron—

$$Fe + S\,O^4Cu = S\,O^4Fe + Cu.$$

Copper dissolves readily in nitric acid. Hydrochloric acid dissolves it with extreme slowness with the aid of heat; but if air have access to the acid surface of the metal, oxygen is absorbed, and a comparatively rapid solution takes place. Concentrated sulphuric acid dissolves the metal with the aid of heat, evolving sulphurous acid and water, and forming cupric sulphate and sulphide.

Aqueous ammonia in presence of air dissolves copper, forming a deep blue solution of $Cu\,O\,(N\,H^3)^2$. Nitrous acid is formed at the same time. The metal acts very little on steam or carbonic acid even at a red heat. Copper forms two basic oxides, and a higher oxide possessing acid properties.

**172. Cuprous Oxide** ($Cu^2O$) occurs as a mineral, and is called, from its form, octohedral copper ore. It can be

prepared artificially by warming a solution of cupric oxide in a mixture of potash and grape-sugar. It then goes down as a red brown powder. Cuprous oxide combines with acids, forming the cuprous salts, which are for the most part insoluble in water but soluble in acids.

The cupric oxide is a black substance obtained by heating metallic copper to redness in contact with the air. For laboratory use it is prepared by heating cupric nitrate to a red heat in an earthen crucible. If too strong heat be applied the oxide clots together and ultimately even melts, giving off some of its oxygen. In analyses cupric oxide is prepared from a solution of one of its salts by adding caustic potash in excess, and boiling the blue precipitate of cupric hydrate until it becomes black by losing its water.

Cupric oxide is reduced by hydrogen or carbonic oxide at a red heat.

Its salts are for the most part blue when combined with water, but they lose that colour when dried.

Copper combines with hydrogen, forming the compound called cuprous hydride ($Cu^2H^2$). It is obtained by the spontaneous decomposition of a solution of cupric hypophosphite. Hydrochloric acid dissolves the hydride, with evolution of hydrogen, and with formation of cuprous chloride—

$$Cu^2H^2 + (ClH)^2 = Cu^2Cl^2 + H^4.$$

Two cupric hydro-carbonates are known. When a salt of copper is decomposed by sodic-carbonate in the cold the precipitate is a hydro-carbonate, and carbonic acid is set free.

Blue copper ore ($Cu^3(CO^3)^2(HO)^2$) is a mineral which occurs in beautiful crystals.

Malachite is found in green masses, which are cut and polished for use as ornaments. Its composition is represented by the formula—

$$Cu^2(CO^3)(HO)^2.$$

Cupric oxalate is obtained as a white precipitate, soluble in acids.

Cupric cyanide is formed by precipitating a solution of cupric sulphate by potassic cyanide. The cyanide dissolves in an excess of potassic cyanide, but undergoes a reduction to cuprous cyanide ($Cu^2C^2N^2$) during the process. This solution of cuprous cyanide is not decomposed by sulphuretted hydrogen.

**Cupric Nitrate** ($Cu(NO^3)^2$). This salt is formed by dissolving metallic copper in nitric acid. It is very soluble and crystallizes, sometimes with three molecules of water, sometimes with six molecules. It cannot be dried without decomposition.

There are two chlorides of copper—a white cuprous chloride ($Cu^2Cl^2$), which dissolves in hydrochloric acid, and a cupric chloride, which crystallizes from water in needle-shaped crystals of the composition $CuCl^2(H^2O)^2$.

With iodine copper forms only one compound, viz. the cuprous iodide $Cu^2I^2$; and when cupric sulphate is mixed with potassic iodide this salt is precipitated, while iodine is liberated at the same time—

$$(CuSO^4)^2 + (KI)^4 = Cu^2I^2 + I^2 + (SO^4K^2)^2.$$

Cupric sulphide is easily and completely thrown down as a black precipitate by the action of sulphuretted hydrogen on a solution of a salt of copper containing free mineral acid. There is also a cuprous sulphide $Cu^2S$, which is formed during the process of smelting.

Cupric sulphate ($CuSO^4(H^2O)^5$), commonly called blue vitriol, is the commonest salt of copper. When the blue crystals are deprived of their water of crystallization by heat they crumble into a white powder, and this dry salt is an excellent re-agent for the discovery of moisture, as it turns blue when brought in contact with any mixture from which it can absorb water.

When hydrochloric acid is added to a blue aqueous solution of cupric sulphate the liquid becomes green, owing to the formation of cupric chloride.

When ammonia is added gradually to a solution of cupric sulphate, a basic sulphate of copper is at first precipitated; and this precipitate dissolves readily on the addition of more ammonia, forming a deep blue solution which may be considered as containing ammonia sulphate combined with ammonia cuprate. The compound can be obtained in crystals, containing $(NH^3)^4 Cu S O^4 H^2 O$.

Ammonia carbonate also precipitates salts of copper, and when added in excess dissolves the precipitate, forming a dark blue liquid.

Cupric phosphate is precipitated on mixing cupric sulphate with hydrodisodic phosphate. The salt appears to contain copper in the place of both sodium and hydrogen of the sodium salt—

$$(P O^4 Na^2 H)^2 + (S O^4 Cu)^3 = (P O^4)^2 Cu^3 + \\ + (S O^4 Na^2)^2 + S O^4 H^2.$$

Arsenious acid forms with cupric oxide a green salt insoluble in water, which can be precipitated by mixing cupric sulphate with an excess of solution of arsenious acid, and then dropping in ammonia until the solution becomes neutral.

**173. Cadmium** (Cd = 112, = 2 vols.) is a comparatively rare metal, which is found associated with zinc, and which presents considerable analogy with zinc. Its density varies from 8.6 to 8.7. It boils at 860°, and its vapour has a density of 56.

Cadmium forms a brown oxide (Cd O), and its salts are colourless unless the acid be coloured, and for the most part crystallizable. Ammonia precipitates white cadmic hydrate, and an excess of ammonia dissolves the precipitate.

Cadmic oxide is not soluble in potash. Potassic cyanide

dissolves it readily, but sulphuretted hydrogen precipitates the whole of the metal as sulphide from this solution.

Cadmic sulphide is a beautiful yellow compound. It does not dissolve in ammonia sulphide. With sulphuric, hydrochloric, or nitric acid, cadmium forms soluble salts.

All the metals of the previous group and of this group are precipitated by zinc from solutions of their salts.

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# CHAPTER XXVIII.

**174. Iron** (Fe = 56; density 7.84). This most important of metals is rarely found native. Its ores are chiefly of two kinds—viz. oxides and carbonates. Among the former the most important are magnetic iron ore ($Fe^3O^4$), specular iron ore or red hæmatite ($Fe^2O^3$), and brown hæmatite $(Fe^2O^3)^2(H^2O)^3$.

Ferrous carbonate sometimes occurs nearly pure, and is then called spathic iron ore. It occurs abundantly mixed with clay and other mineral bodies, and is then called clay-iron stone. The black band is ferrous carbonate containing bituminous matter.

Many ores of iron are deprived of their most volatile constituents by roasting, before they are introduced into the furnace for reduction.

The **Blast Furnace** is a gigantic structure 50 to 80 feet high, containing alternate strata of coal or coke and iron ore, mixed with limestone, which are constantly supplied at the top of the furnace, and gradually sink down until they ultimately run out at the bottom of the furnace, partly as molten cast-iron, partly as liquid calcic and aluminic silicates, &c., called slag. Air is forced in at the bottom of the furnace to support

the combustion of the coals, and it is found advantageous to heat this blast of air to about the melting-point of lead before it enters the furnace. Hot carbonic acid and steam pass upwards together with the nitrogen of the air, and coming in contact with white-hot carbon the two former gases are reduced to carbonic oxide and hydrogen. As soon as a stratum of ore thrown in at top has descended sufficiently to be heated by the hot mixture of nitrogen, carbonic oxide, and hydrogen, it becomes reduced to spongy metallic iron, which is mixed with the clay and limestone, &c. which were present with it. The gases take up oxygen from the ore and pass over into carbonic acid and steam, but retain usually a good deal of unburnt gases.

The spongy metallic iron, mixed with stones and clay, &c., descends to hotter parts of the furnace, where the iron combines with carbon, forming liquid carburet, while the lime unites with the silica and alumina, &c., forming the liquid slag.

The liquid carburet of iron settles at the bottom of the deep hearth at the bottom of the furnace, from which it is let out occasionally by the removal of a plug of clay; while the slag runs off from the top of the hearth, in proportion as it is formed.

While the iron is combining with carbon it also combines with silicon, sulphur, phosphorus, &c., and these substances are present in crude cast-iron (called pig), in various proportions, besides occasional admixtures of manganese, aluminium, and other metals, which are not to be regarded as impurities.

Liquid iron appears to take up a little more than 5 per cent. of carbon, corresponding to the compound $Fe^4C$, and when the molten compound is rapidly cooled a "white" crystalline mass is obtained of extreme hardness and brittleness.

If the molten carburet be allowed to cool slowly, some of the carbon crystallizes out on its surface in scales like plumbago, while some particles of carbon remain dispersed among

the crystals of iron, forming a mass of "grey" or "mottled" fracture. The presence of certain foreign bodies—such as manganese, sulphur, or phosphorus—in the carburet prevents this separation of the carbon in slow cooling. Spiegeleisen is a kind of cast-iron containing 5 per cent. or more of manganese, and no carbon crystallizes out from it even on the slowest cooling.

When white iron is heated with hydrochloric acid it dissolves with evolution of hydrogen, possessing a very fœtid odour, and few or no particles of carbon are found in the liquid when the iron has dissolved. The hydrogen owes its smell to the presence in it of volatile compounds of carbon and hydrogen.

When grey cast-iron is dissolved in the acid, it leaves numerous fragments of carbon, which cannot be driven off by the action of the acid, and the hydrogen which is evolved contains very little of the volatile compounds of carbon and hydrogen.

The explanation of these different results is to be found in the fact that the hydrogen which is being evolved from the hydric chloride is able to change places with iron of the compound $Fe^4C$, and thus to pass off in combination with carbon, but cannot combine with carbon which is present in the state of graphite.

The carbon in white iron is held in chemical combination with the iron, and passes off in combination with hydrogen; whereas the carbon of grey iron is mostly uncombined with iron, and remains unchanged when the iron is dissolved.

White iron melts more easily and rapidly than grey iron, as this latter has gradually to combine with the carbon which is mechanically mixed with it, and to reproduce the fusible carburet of iron.

The specific gravity of cast-iron varies from 7 to 7.25, and is sometimes even higher. Its tensile strength varies from

that which will bear a strain of 6 tons on the square inch, up to more than double that strength.

The stiffness of cast-iron is measured by the weight which a straight pillar of it having one square inch thickness can support. It varies from 22 tons to upwards of 50 tons.

The lighter varieties of cast-iron are, both as regards tenacity and stiffness, inferior to the denser varieties, and the easiest way of judging of the strength of any specimen of cast-iron is accordingly to take its specific gravity.

Large and massive castings of iron take so long to cool that the particles have time to arrange themselves in large crystals, whereby the strength of the mass is diminished.

Castings of great hardness on the surface are obtained by using an iron mould, which 'chills' the particles next to it so rapidly that the carbon remains in great part combined or very intimately mixed with the iron.

**175.** In order to make **Malleable Iron** from pig-iron a good quality should be selected and melted in a shallow hearth over which the flames from a reverberatory furnace are playing. Air is allowed to pass into the molten mass and to oxidize its surface, forming carbonic acid and ferric oxide, and this oxide is stirred about by a workman so as to come in contact with the molten carburet of iron below. At the end of the process the mass is heated by itself for some time, all air being excluded from the furnace.

Carbon is thus burnt out of the carburet of iron, partly by the direct action of atmospheric oxygen, partly by the action of the oxygen of ferric oxide, formed on the surface of the mass; and the mass gets thicker and more tenacious in proportion as the carbon is more and more fully removed, until at last it is rolled about on the hearth in the form of a large ball or 'bloom' of soft sticky iron, adhering to the end of the workman's iron rod. This process of decarbonizing iron is called 'puddling.'

These blooms are brought while still hot under a steam hammer or a powerful press, so as to beat or press out the slag and other impurities which they contain, and to unite the particles of iron uniformly together. By repeatedly heating the iron and working it about its quality is further improved if necessary. In many cases it is customary to subject cast-iron to a process of refining, for the removal of the greater quantity of its impurities previous to puddling. A more rapid process of decarbonizing iron has been introduced of late years by M. Bessemer, and has been found very advantageous when applied to certain qualities of iron. Bessemer runs the liquid cast-iron into a large pot of refractory clay, and blows air rapidly through it. Intense heat is evolved, partly by the combustion of the carbon, partly also by combustion of iron; and the fluid mass is kept in violent agitation by the nitrogen and carbonic oxide which are passing through it. In this manner the carbon and silicon are completely removed, and the temperature is so high that the metallic iron is left in a fluid state. It is generally run into moulds, in which it is mixed with spiegeleisen in sufficient quantity to yield a metal with about one-half per cent. of carbon.

Another process of decarbonization is that by which so-called **Malleable Cast-iron** is made. It consists in packing the cast-iron utensils into a stoneware vessel, and filling up with hæmatite or smithy scales the spaces which are left. The whole is then kept at a good red heat for several days, or even for a week, and the carbon gradually passes out from the iron in the form of carbonic oxide.

This result is owing to the action of carbonic acid and steam on the carbon of the cast-iron. These gases are reduced by carbon at a red heat—

$$C + Co^2 = (C\,O)^2; \quad C + H^2O = Co + H^2;$$

and the products formed (Co + H) come in contact with

the ferric oxide which surrounds the cast-iron, and are oxidized by it into carbonic acid and steam, which again penetrate into the cast-iron, and carry out more of its carbon. It is scarcely practicable to remove by this process the carbon to the depth of more than half an inch from the surface of the casting.

Pure metallic iron is a very soft metal, and is valuable for purposes in which tenacity alone is required. A bar of wrought iron of one square inch section ought to carry a dependent weight of 20 tons, and the best specimens of iron carry considerably more.

**Iron** dissolves readily in dilute mineral acids, but strong nitric acid covers it with a film of anhydrous ferric oxide, which prevents the further action of the acid, or even of dilute nitric acid. This film is easily removed by the action of reducing agents, and the passive iron is thereby rendered active again, and capable of dissolving in dilute nitric acid.

**176.** Metallic iron gradually absorbs oxygen when exposed to air in presence of moisture, forming ferric oxide, commonly called rust; and the presence of a particle of oxide on the surface of iron causes it to oxidize more rapidly than it otherwise would do. The presence of a particle of copper or tin, or of any one of the metals hitherto described, exerts a similar action in accelerating the process of rusting. Iron does not rust when its surface is moistened with a solution of sodic carbonate, or any other alkaline liquid.

It decomposes steam at a red heat, forming magnetic oxide of iron. Some of the steam passes over with the hydrogen undecomposed. At a white heat it even liberates potassium from potassic hydrate.

Iron also reduces carbonic acid in a similar manner at a red heat, forming carbonic oxide, which passes over with undecomposed carbonic acid.

Carbonic oxide is also decomposed by metallic iron at a red heat, carbon being taken up by the iron, and carbonic acid being formed. It is probable that in this process ferrous carburet and oxide are simultaneously formed by the absorption of carbonic oxide, and that the ferrous oxide is subsequently reduced by a second molecule of carbonic oxide.

177. **Steel** is manufactured largely by this process, which is called cementation. Plates of good soft iron are arranged in a stoneware box with alternate layers of charcoal, and the box is closed and heated for several days to a bright red heat. Carbon gradually penetrates into the iron, and the process is usually continued until about 1.5 per cent. of carbon have been taken up. The oxygen of the air enclosed in the box forms carbonic oxide, and this gas penetrates into the iron. Two molecules of carbonic oxide give up an atom of carbon to the iron, while carbonic acid passes out. The carbonic acid which is formed in the process is reduced again by the surrounding charcoal to carbonic oxide, which carries another atom of carbon into the iron. The steel first obtained in this manner is called 'blistered steel,' from the appearance which it presents; and its composition is far from uniform throughout each plate. It is subjected to various mechanical processes, of which the effect is to mix its various parts more uniformly; but the only process which attains this object completely is fusion, and cast-steel is accordingly the most homogeneous variety of that valuable compound. Steel can be hardened by the process of tempering, and softened again by so-called annealing. The higher the temperature from which steel is suddenly cooled by immersion in oil the greater is its hardness or so called temper; and by again heating the steel utensil and allowing it to cool slowly it is softened or annealed. Steel is also valuable for its elasticity.

**178.** Iron forms two basic oxides—ferrous oxide (Fe O) and ferric oxide ($Fe^2 O^3$). It also forms an acid with more oxygen.

**Ferrous Oxide** is obtained in combination with water by the action of potash or ammonia in a solution of ferrous sulphate. The precipitate is a white hydrate, and it absorbs oxygen with great rapidity, turning first blue and ultimately brown. The hydrate dissolves in ammonia chloride.

**Ferric Oxide** is found in brilliant crystals called specular iron ore. It is best prepared artificially by precipitating ferric chloride or ferric sulphate by ammonia, and heating the precipitate after due washing. Potash combines with the sesquioxide when used for its precipitation.

There are several hydrates. The precipitate first formed by an excess of ammonia is said to be the normal hydrate $Fe^2 O^3 H^6$, but it speedily loses half its water—

$$(Fe^2 O^3 H^6)^2 - (H^2 O)^3 = Fe^4 O^9 H^6.$$

There are also oxy hydrates of the respective composition $Fe^2 O^4 H^2$ and $Fe^2 O^5 H^4$.

Magnetic oxide of iron is considered to be a compound of ferrous oxide with ferric oxide ($Fe^2 O^3$ Fe O).

There are many evidences of the fact that ferrous oxide is a stronger base than the sesquioxide. Thus, hydrated ferrous oxide added to a solution of ferric sulphate precipitates the sesquioxide. Barytic carbonate precipitates ferric oxide from a solution of the ferric chloride, while carbonic acid is evolved—

$$(C O^3 Ba)^3 + Cl^6 Fe^2 = (C O^2)^3 + Fe^2 O^3 + (Ba Cl^2)^3.$$

The precipitated oxide contains water in combination.

The baryta salt has no action upon ferrous chloride under similar circumstances.

**179. Ferrous Cyanide** is chiefly known in combination with other cyanides. There are, however, two important blue compounds, which consist of iron and cyanogen.

One of these is called Prussian blue, and gave rise to the name prussic acid. It is formed by mixing a solution of potassic ferrocyanide ($Fe\,Cy^6\,K^4$) with a solution of a ferric salt, and potassic ferrocyanide constitutes an excellent reagent for iron when present in the form of a sesquisalt. With a solution of ferric chloride the reaction occurs thus, $(Fe\,Cy^6\,K^4)^3 + (Fe^2\,Cl^6)^2 = Fe^7\,Cy^{18} + (K\,Cl)^{12}$; dilute mineral acids have no action on Prussian blue, but it is readily decomposed by alkalies. Thus, potash reproduces potassic ferrocyanide from it, and precipitates ferric oxide—

$$Fe^7\,Cy^{18} + (H\,K\,O)^{12} = (Fe\,Cy^6\,K^4)^3 + (Fe^2\,O^3)^2 + (H^2O)^6.$$

The other blue compound is usually called Turnbull's blue. It is precipitated by mixing a solution of potassic ferrycyanide with a ferrous salt—

$$Fe^2\,Cy^{12}\,K^6 + (Fe\,Cl^2)^3 = Fe^5\,Cy^{12} + (K\,Cl)^6.$$

With potash it reacts thus—

$$Fe^5\,Cy^{12} + (H\,K\,O)^8 = (Fe\,Cy^6\,K^4)^2 + Fe^2\,O^6\,H^6 + Fe\,O^2\,H^2.$$

Ferrous cyanide can be obtained in combination with prussic acid, forming a white crystalline compound called hydro-ferrocyanic acid ($Fe\,Cy^6\,H^4$). This acid is precipitated from a solution of potassic ferrocyanide by the addition of hydrochloric acid and ether. It speedily absorbs oxygen from the air and turns blue.

Ferrous carbonate ($C\,O^3\,Fe$) is precipitated by the action of an alkaline carbonate on ferrous sulphate. It is a white powder which rapidly absorbs oxygen from the air, giving off its carbonic acid and becoming ferric oxide. The salt dissolves in water containing free carbonate acid, and is present in this form in the water from some springs, from which ferric oxide is deposited by the evaporation of carbonic acid into the air and the absorbtion of oxygen.

**180. Ferrous Chloride** ($Fe\,Cl^2$) is obtained in solution by dissolving the metal in hydrochloric acid. Like most of the ferrous salts this compound has a pale green yellow. When

exposed to the air it gradually turns yellow by absorption of oxygen, and deposits a ferric oxy chloride. Ferrous chloride can be obtained as a white salt by evaporating its solution to dryness and heating the residue.

**Ferric Chloride** ($Fe^2Cl^6$) is best obtained by burning iron wire in an excess of dry chlorine. It is deposited in the form of shining scales, which can easily be volatilized by heat. Once dissolved in water the salt cannot be recovered by evaporation, as its solution decomposes very readily, into hydrochloric acid which goes away, and ferric oxide which remains behind. A solution of this or of any other ferric salt, provided the acid be not possessed of reducing properties, withstands boiling without undergoing any reduction to ferrous salt.

Iodine seems only to form at ordinary temperatures one compound with iron, a ferrous iodide, for when a solution of ferric chloride is mixed with potassic iodide, iodine is set free; $Fe^2Cl^6 + (KI)^6 = (FeI^2)^2 + I^2 + (KCl)^6$.

There are two definite sulphides of iron—a black ferrous sulphide (Fe S) and a yellow disulphide ($FeS^2$), commonly called pyrites. Iron burns with considerable intensity in the vapour of sulphur, forming the ferrous sulphide. It is readily fusible and dissolves in dilute sulphuric or hydrochloric acid with evolution of sulphuretted hydrogen—

$$FeS + (HCl)^2 = FeCl^2 + H^2S.$$

Sulphuretted hydrogen gas does not decompose the ferrous salts, but on the addition of ammonia a black precipitate, consisting of ferrous sulphide combined with water, is formed. This precipitate dissolves very easily in acids, and rapidly absorbs oxygen from the air, the iron becoming ferric oxide, while the sulphur remains for the most part unoxidized.

Ferric salts are reduced by sulphuretted hydrogen with deposition of sulphur, thus—

$$Fe^2Cl^6 + H^2S = (FeCl^2)^2 + (HCl)^2 + S.$$

Pyrites is of considerable value as a source of sulphur, for the preparation of sulphuric acid. It is sometimes decomposed by a process of distillation, by which less than half the sulphur is expelled from the pyrites. It is more common to roast the pyrites so as to oxidize both its constituents, leading the sulphurous acid into the lead chamber. Ferric disulphide is not dissolved by hydrochloric or by dilute sulphuric acid.

**181. Ferrous Sulphate** ($FeSO^4$), commonly called green vitriol or copperas, is formed when iron dissolves in dilute sulphuric acid. It is prepared on a large scale by the action of air upon moist pyrites.

Common green vitriol contains seven molecules of water of crystallization ($SO^4Fe(H^2O)^7$), which can be driven off by heat. Stronger heat decomposes the dry sulphate, sulphurous acid coming off and ferric di-oxy sulphate being formed—

$$(FeSO^4)^2 = SO^2 + Fe^2O^2SO^4.$$

On further heating, this oxy salt is in its turn decomposed, anhydrous sulphuric acid coming off and red ferric oxide remaining behind.

Ferrous sulphate can also be obtained in combination with 4 or 3 or 2 molecules of water of crystallization. The crystals of the ordinary salt absorb oxygen from the air and turn brown, being transformed into the ferric oxy disulphate $Fe^2(OSO^4)^2$.

Ferrous sulphate combines with potassic sulphate, forming the double salt $FeK^2(SO^4)^2(H^2O)^6$. Similar double salts are formed with other alkalies.

Normal **Ferric Sulphate** ($Fe^2(SO^4)^3$) can be obtained by dividing a convenient quantity of oil of vitriol into three equal portions, saturating two of these portions, after dilution, with metallic iron, then adding the third portion to this solution and evaporating down to dryness with an excess of

nitric acid. The salt is white. It gives off its sulphuric acid in the anhydrous state on heating.

Ferric sulphate combines with ammonia sulphate, forming a salt which crystallizes in beautiful violet-coloured octohedrons; $(S O^4)^4 Fe^2 (N H^4)^2 (H^2 O)^{24}$.

Ferrous phosphate ($(P O^4)^2 Fe^3$) can be obtained as a white powder by double decomposition; it is found in combination with water as a mineral called vivianite.

Ferric phosphate ($Fe P O^4 (H^2 O)^2$) is precipitated as a brownish white gelatinous salt on mixing a ferric salt with a neutral and soluble phosphate. The salt dissolves in mineral acids but is not dissolved by acetic acid, and its solution in hydrochloric acid is precipitated by the addition of ammonia acetate, the hydrochloric acid being neutralized by the ammonia, and acetic acid liberated in its stead.

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# CHAPTER XXIX.

**182. Aluminium** (Al = 27.5; density 2.56 to 2.67) is prepared by the action of metallic sodium in the double chloride of aluminium and sodium.

It is a blueish-white metal, remarkable for its great lightness. A bar of aluminium, when suspended by string, rings with a clear and musical note when gently tapped. The metal can be drawn into fine wire or rolled into plates. The surface becomes dull when the metal is long exposed to the air. Nitric acid in a dilute state has scarcely any action on aluminium, but hydrochloric acid dissolves it rapidly with evolution of hydrogen, forming aluminic chloride ($Al^2 Cl^6$). Dilute sulphuric acid dissolves it with difficulty.

Aluminium can be melted in an open crucible without oxidation, and cast into moulds. It forms with copper a very beautiful alloy of great strength and elasticity, and of the colour of gold. This aluminium bronze contains 90 per cent. of copper and 10 of aluminium.

**183.** There is only one oxide of aluminium, the so-called **Alumina**, which occurs crystallized as corundum. The close analogy of alumina with ferric oxide has decided chemists to class it among the sesquioxides, and to give it the formula $Al^2O^3$.

It is best obtained in a state of purity from commercial sodic-aluminate. The solution of this compound is acidulated by hydrochloric acid, evaporated to dryness and heated with frequent stirring. On washing the mass with water pure alumina is left behind. Alumina can be precipitated as a hydrate by ammonia, or ammonia carbonate from a solution of one of its salts, but from its gelatinous consistency it is a troublesome precipitate to wash. As long as it retains water in combination it can be easily dissolved by caustic potash or by acids, but it is insoluble in hydrochloric acid after having been exposed to a red heat. Potassic hydrate, however, combines with it at a red heat, and renders it again soluble in acids. Alumina is not reduced by carbon or hydrogen, even at the highest temperatures.

It combines with many colouring matters, forming solid compounds, by the aid of which the colours are fixed upon cotton or linen. When exerting this action alumina is termed a mordant. A very common material for mordanting consists of aluminic sulphate (either pure or combined with ammonia sulphate), in which two-thirds of the sulphuric acid are replaced by acetic acid. This double salt, consisting of alumina combined partly with acetic acid, partly with sulphuric acid, very readily allows its acetic acid to escape by evaporation, while aluminic hydrosulphate is left behind.

A piece of calico moistened with a solution of the salt and hung up in a warm and moist air becomes impregnated with aluminic hydrosulphate by the process called aging, which is nothing else than an evaporation of acetic acid.

If subsequently immersed in a solution of madder dye, the cloth becomes dyed by a combination of the mordant contained in it with the colouring matter.

**184. Aluminic Chloride** ($Al^2Cl^6$) cannot be formed by driving off the water from a solution of the salt, as it decomposes during that operation into hydrochloric acid and alumina. Finely-divided alumina is prepared from sodic aluminate, and intimately mixed with coal-dust. The mixture is heated to bright redness in a fire-clay tube, through which chlorine is passing. Carbonic oxide escapes while aluminic chloride sublimes up to the colder parts of the tube—

$$Al^2O^3 + C^3 + Cl^6 = Al^2Cl^6 + (CO)^3.$$

The vapour of aluminic chloride is 134 times as heavy as hydrogen, as can be seen from the fact that $Al^2Cl^6$ occupies two volumes.

Aluminium does not combine with sulphur in the wet way. Ammonia sulphide added to a solution of a salt of alumina precipitates the white aluminic hydrate, while sulphuretted hydrogen is liberated—

$$Al^2Cl^6 + ((NH^4)^2S)^3 + (H^2O)^6 = Al^2O^6H^6 + \\ + (H^2S)^3 + (ClNH^4)^6.$$

**185. Aluminic Sulphate** is prepared by heating clay with sulphuric acid, and precipitating, as Prussian blue, the iron which dissolves with it. The salt crystallizes with water—

$$Al^2(SO^4)^3(H^2O)^{18}.$$

Its solution is intensely acid. The double salt containing aluminic sulphate, combined with potassic sulphate, has long been known by the name of alum. It crystallizes in regular octohedrons, containing 24 molecules of water—

$$Al^2K^2(SO^4)^4(H^2O)^{24}.$$

Of late years it has been to a great extent superseded in this country by ammonia alum—

$$Al^2(NH^4)^2(SO^4)^4(H^2O)^{24}.$$

Sodium forms a double sulphate similar to them, and having the same crystalline form.

These alums cannot be separated by crystallization; and a crystal of one of them can be got to grow regularly in a solution of another alum, just as well as in a solution of the same kind; the particles of one kind of alum arranging themselves symmetrically with those of another kind.

Ferric sulphate, chromic sulphate, and manganic sulphate form double salts with the sulphates of the alkalies, perfectly similar in constitution and in crystalline form to the alums, and capable of crystallizing with them in the same crystals.

Aluminic phosphate ($PO^4Al$) is precipitated in the form of a white gelatinous mass by the decomposition of alum by hydrodisodic phosphate. It dissolves in acids or in potash, and so closely resembles alumina that some care is required for the detection of the phosphoric acid in it. Ammonia nitromolybdate affords the most rapid means of discovering phosphoric acid when combined with alumina.

**186.** Silica occurs very commonly in combination with alumina and other bases in minerals, and the various kinds of clay are products of the gradual decomposition of felspar and similar double silicates, by the action of carbonic acid, water, and ammonia. Common felspar is represented by the formula $(SiO^2)^6Al^2O^3K^2O$. In some varieties the potash is more or less completely replaced by soda, while ferric oxide is generally present in small quantity, taking the place of some of the alumina. The alkali is gradually dissolved out from these minerals while they crumble down to a soft mass, and most kinds of clay still retain some of the alkali of the original rock in combination.

One of the most important properties of clay is that of

absorbing water and forming with it a soft pasty compound, through which the rootlets of plants can work their way, and from which they can take up water containing potash, ammonia, phosphoric acid, &c., in solution, for their vital functions. Clay combines in a similar loose manner with ammonia, and holds it, like the water, in readiness for the plants. Some clays are so tenacious as to retain too much wet on the surface of the soil, and to prevent its draining down to the subsoil. These are very justly termed "cold," for much of the heat from the sun's rays which fall on such a wet soil is absorbed in evaporating the water, and lost to the plants whose growth is dependent upon it. Many such clays are greatly improved by burning, which not only diminishes their tenacity but also renders the alkali remaining in them more soluble.

The most refractory clays, such as Stourbridge clay, which is used for the manufacture of fire-bricks, are not only those most free from alkalies, but also those containing the largest proportion of silica, such as $(Si\,O^2)^6\,Al^2\,O^3$; whilst many clays have a composition approaching more nearly to the formula $(Si\,O^2)^3\,Al^2\,O^3$.

Earthenware, pottery, and bricks are made of plastic clay, the latter having a considerable proportion of sand mixed up with the clay before it is moulded into shape.

Stoneware and china are made of superior qualities of clay, and glazed by the addition of felspar, in sufficient quantity to form at the high temperature of the kiln a glass which fills up the pores of the clay.

**187. Chromium** ($Cr = 52.5$). This metal has been reduced from its oxide by charcoal at a very high temperature, and by potassium from its chloride. It has, however, been but little studied as yet.

The mineral from which chromium compounds are usually prepared is the chrome iron-stone ($Cr^2\,Fe\,O^4$).

Cromium forms three distinct oxides, and probably a fourth. Two of its oxides are bases—viz. chromous oxide ($CrO$) and chromic oxide ($Cr^2O^3$). The third is an acid ($CrO^3$), chromic acid.

Chromous oxide is analogous in its salts to ferrous oxide, but these salts absorb oxygen far more rapidly and retain it more forcibly than the corresponding salts of iron.

Chromic oxide is a bright green powder, much valued as a paint. It is obtained by heating its hydrate, precipitated by excess of ammonia from a solution of chromic chloride. Chromic oxide forms green salts under special conditions; another class of salts corresponding to this oxide are formed, distinguishable from the above by their violet colour and by the power of crystallizing, which the green salts do not possess.

Chromic hydrate dissolves in potash, and is precipitated from that solution by boiling.

In order to separate it from alumina the two oxides should be dissolved in cold potash in excess, and the chromic oxide oxidised into chromic acid by the action of chlorine. After acidulation of the liquid by hydrochloric acid the alumina can be precipitated alone by ammonia carbonate.

Chromic oxide behaves like alumina to ammonia sulphide; for the precipitate produced by that reagent in the solution of a chromic salt is chromic hydrate, while sulphuretted hydrogen is liberated—

$$Cr^2(SO^4)^3 + ((NH^4)^2S)^3 + (H^2O)^6 = Cr^2O^6H^6 + \\ + (SO^4(HN^4)^2)^3 + (H^2S)^3.$$

**188. Chromic Acid** ($CrO^3$) can be obtained in the form of crimson needles by leading the vapour of chromic fluoride ($CrFl^6$) into a moist platinum crucible.

It is a bibasic acid, and forms a neutral potash salt ($CrO^4K^2$), isomorphous with neutral potassic sulphate. Potassic chromate is yellow, and its colouring power is so great as

*to* afford a delicate test for the presence of the salt in a solution.

Potassic dichromate, commonly called red chromate, is the salt most commonly manufactured. Its composition is represented by the formula $Cr^2O^7K^2$.

Chromic acid is reduced by boiling with strong aqueous hydrochloric acid, a green colour taking the place of the original red one. Chlorine is given off, and chromic chloride is left in solution—

$$CrO^3 + (HCl)^6 = CrCl^3 + Cl^3 + (H^2O)^3.$$

A similar reduction with precipitation of sulphur is effected by sulphuretted hydrogen, in liquids containing chromic acid mixed with a mineral acid—

$$(CrO^3)^2 + (HCl)^6 + (H^2S)^3 = Cr^2Cl^6 + S^3 + (H^2O)^6.$$

When a salt of chromic acid is heated with strong sulphuric acid and sodic chloride, a red vapour consisting of chlorochromic acid is given off. The reaction is thus represented—

$$CrO^4K^2 + (NaCl)^2 + (SO^4H^2)^2 = CrO^2Cl^2 + + SO^4K^2 + SO^4Na^2 + (H^2O)^2.$$

An excess of oil of vitriol is needed in the reaction in order to combine with the water which is formed.

When chromic acid is heated with strong sulphuric acid it gives off half its oxygen, forming chromic sulphate—

$$(CrO^3)^2 + (SO^4H^2)^3 = Cr^2(SO^4)^3 + O^3 + (H^2O)^3.$$

This mixture affords one of the most powerful means of oxidizing carbon at comparatively low temperatures.

Chromic acid forms a yellow neutral salt with baryta which is insoluble in water but soluble in hydrochloric acid, also a red barytic dichromate ($Cr^2O^7Ba$), which dissolves in water.

The neutral argentic chromate is a crimson salt insoluble in water but soluble in nitric acid.

Neutral plumbic chromate ($CrO^4Pb$) is a yellow insoluble salt much used as a yellow paint.

There is also a basic plumbic chromate of an orange colour.

**189.** Two chlorides of chromium are known—viz. the chromous chloride $Cr Cl^2$, a white powder obtained by heating chromic chloride in a stream of hydrogen, and the chromic chloride $Cr^2 Cl^6$, a pink salt which becomes green on combining with water.

Chlorochromic acid ($Cr O^2 Cl^2$), mentioned above, is one of the most important compounds theoretically. Its molecule occupies two volumes in the state of vapour—

$$Cr O^2 Cl^2 = 2 \text{ vols.}$$

and is accordingly 77·75 times as heavy as hydrogen. The red vapour condenses to a heavy oily liquid, having a boiling-point at 118°. Chlorochromic acid is dissolved by water with decomposition ($Cr O^2 Cl^2 + H^2 O = Cr O^3 + (H Cl)^2$), and cannot be recovered by evaporation.

Chromic fluoride is easily formed by distilling red potassic chromate with ammonia fluoride and an excess of strong sulphuric acid in a platinum retort—

$$Cr^2 O^7 K^2 + (N H^4 F)^{12} + (S O^4 H^2)^7 = (Cr F^6)^2 + + S O^4 K^2 + (S O^4 (N H^4)^2)^6 + (H^2 O)^7.$$

**190. Uranium** (Ur = 120). The chief ore of uranium is pitch-blende. The metal forms a protoxide analogous to chromous oxide, which does not give up its oxygen at a red heat to hydrogen. It also forms a yellow uranic oxide ($Ur^2 O^3$), which is soluble in carbonate of ammonia, hydrochloric nitric, or sulphuric acid. The sesquioxide forms an insoluble phosphate. Uranium is used for preparing a beautiful yellow glass with a tinge of green, and which is remarkable for its fluorescence.

# CHAPTER XXX.

**191. Cobalt** (Co = 58.5) is found associated with nickel, arsenic, and some other metals.

It can be reduced from its oxides by charcoal at a high temperature, and can with difficulty be melted to a compact button of a specific gravity of 8.95. Cobalt is slightly magnetic.

It forms a cobaltous oxide Co O, which is a brown powder, when obtained by heating a higher oxide in a stream of carbonic acid. The compounds which protoxide of cobalt forms by reacting on acids are generally blue when free from water, and not unfrequently of the same colour in presence of water mixed with a strong mineral acid. In combination with water they are generally red. Ammonia sulphide added to one of them forms a black precipitate of cobaltous sulphide, which is not soluble in hydrochloric acid. Potash precipitates a pink cobaltous hydrate—

$$Co\,O^2\,H^2,$$

which rapidly absorbs oxygen from the air and turns to a dingy green colour.

Ammonia forms a similar precipitate, but an excess of the reagent dissolves it, and the solution gradually becomes brown in contact with air, by absorbing oxygen. If ammonia chloride be present in sufficient quantity potash does not precipitate the solution.

Barytic carbonate does not decompose a solution of cobaltous chloride in the cold, but if chlorine be passed through the mixture a cobaltic chloride is formed which is entirely decomposed by the barytic salt—

$$(Co\,Cl^3)^2 + (Co^3\,Ba)^3 = Co^2\,O^3 + (C\,O^2)^3 + (Ba\,Cl^2)^3.$$

A mixture of cobaltic oxide and strong hydrochloric acid gives off chlorine when heated and forms a solution of cobaltous chloride.

Potassic cyanide precipitates cobaltous salts, forming cobaltous cyanide, but this precipitate dissolves readily in an excess of potassic cyanide, and the double cyanide thus obtained decomposes prussic acid at the boiling-point, evolving hydrogen and forming a double salt of great stability, and having the empyrical formula $Co^2 Cy^{12} K^6$, which is explained as being made up of cobaltic cyanide ($Co^2 Cy^6$) combined with $Cy^6 K^6$. Cobalt can easily be detected by the bright blue colour which its oxide imparts at a high temperature to glass, to borax, or any other salts of the alkalies, or to alumina. With zinc oxide it forms a green compound which is used as a paint, and with magnesia a pale pink compound.

Smalt is the powder of a blue glass coloured by cobalt, and Thenard's blue is a compound of oxide of cobalt with phosphoric acid and alumina.

Cobaltic oxide is a black powder which dissolves in sulphuric acid with evolution of oxygen, in hydrochloric acid with evolution of chlorine, and is very slightly acted upon by nitric acid.

Cobaltous chloride can be obtained in the form of blue scaly crystals when dry. It is deposited from aqueous solution, in combination with six molecules of water, in ruby red crystals. The red solution becomes blue on the addition of a strong mineral acid, but recovers its red colour on dilution.

Cobaltous sulphate ($S O^4 Co (H^2 O)^7$) is an easily crystallizable salt, which combines with potassic sulphate, forming the salt $(S O^4)^2 Co K^2 (H^2 O)^6$.

**192. Nickel** (Ni = 58.5) is remarkable for its great analogy to cobalt. It is chiefly made for the sake of an alloy called German silver, which contains copper, zinc, and nickel

*in* various proportions, generally approaching to two parts of copper, one of zinc, and one of nickel.

Nickel forms a nickelous oxide (Ni O), of which the salts are green in presence of water and yellow when dry.

There is also a nickelic oxide ($Ni^2 O^3$), of which no salts are known.

Nickelous chloride is a beautiful green salt, which crystallizes with nine molecules of water.

Its solution in water is not decomposed in the cold by barytic carbonate, either by itself or in presence of chlorine; and it can accordingly be purified from cobalt by the action of these reagents.

Potash gives a green precipitate of nickelous hydrate. Ammonia gives a similar precipitate, but when added in excess dissolves the precipitate, forming a blue solution. This solution of nickel in ammonia is precipitated by the addition of an excess of potash.

Potassic cyanide precipitates nickel cyanide, and when added in excess dissolves the cyanide. Mercuric oxide precipitates all the nickel from this solution as oxide, but it has no action on the solution of the potassio cobaltic cyanide $Co^2 Cy^{12} K^6$.

Ammonia sulphide precipitates black nickel sulphide, which dissolves in hydrochloric acid. It also dissolves to some extent in an excess of ammonia sulphide, forming a dark brown solution.

Nickel sulphate is a green salt, which crystallizes readily from water with the composition $S O^4 Ni (H^2 O)^7$. These crystals have the same form as those of ferrous sulphate and cobaltous sulphate. Nickel sulphate combines with potassic sulphate, forming the salt $(S O^4)^2 Ni K^2 (H^2 O)^6$.

**193. Manganese** ($Mn = 55$; sp. gr. 8). The most important ore of this metal is the dioxide $Mn O^2$, which is usually called 'manganese' in commerce.

The metal can be reduced from its oxide by charcoal at a high temperature, and melts with difficulty into a button. Hydrogen does not reduce the metal from its chloride, whereas the chlorides of iron, cobalt, and nickel are reduced by hydrogen to the metallic state.

Manganese remains bright when kept in dry air, but in presence of moisture it gradually crumbles down to a brown oxide. The only alloy of the metal which is of commercial value is spiegeleisen, which consists essentially of iron, with 5 to 15 per cent. of manganese, and 5 per cent. of carbon.

**Manganese** forms five definite oxides, two of which—the manganous oxide and manganic oxide—are bases, and are known in the free state as well as in compounds.

The third oxide is only known in the free state, being neither an acid nor a base. It is called manganic dioxide, or peroxide.

The two highest oxides are manganic acid ($Mn O^3$) and permanganic acid ($Mn^2 O^7$). These are only known in combination with bases in the manganates (such as $K^2 Mn O^4$), and permanganates (such as $K^2 Mn^2 O^8$).

Manganous oxide can be obtained by heating its carbonate in an atmosphere containing no free oxygen. It is analogous to ferrous oxide in its salts, and they are of a faint pink colour in presence of water.

Manganous hydrate ($Mn O^2 H^2$) is precipitated by potash from a solution of a manganous salt. It dissolves readily in ammonia chloride, and in this solution gradually absorbs oxygen, and goes down as manganic hydrate.

**Manganic Oxide** ($Mn^2 O^3$) is found in crystals, and is termed brannite by mineralogists. It is analogous to ferric oxide in its salts, but a solution of any of its salts is reduced by boiling to the corresponding manganous salt; thus manganic sulphate ($Mn^2 (S O^4)^3$) is reduced to manganous sulphate ($Mn S O^4$).

Manganic dioxide is a black compound, insoluble in nitric acid, soluble in strong hydrochloric acid at a high temperature, with evolution of chlorine and formation of manganous chloride; $Mn O^2 + (H Cl)^4 = Mn Cl^2 + Cl^2 + (H^2 O)^2$. It is soluble also in strong sulphuric acid at a high temperature, with evolution of oxygen.

It can be prepared by heating manganous carbonate with constant stirring in contact with the air, as long as its colour continues to become darker. The black powder thus formed is a compound of manganic dioxide and manganous oxide, and the latter oxide can be dissolved out from it by nitric acid.

Manganic dioxide gives off one-third of its oxygen at a strong red heat, leaving a brown powder ($Mn^3 O^4$), which corresponds in composition to the magnetic oxide of iron—

$$(Mn O^2)^3 = Mn^3 O^4 + O^2.$$

**194.** Manganous carbonate is found crystallized in the same form as ferrous carbonate. It is precipitated as a white powder by the action of sodic carbonate on manganous chloride, but it always loses a little carbonic acid, and acquires a brownish colour during the operation of drying.

**Manganous Chloride** ($Mn Cl^2$) is formed in large quantities in the preparation of chlorine, by dissolving manganic peroxide in hydrochloric acid.

It can be obtained nearly pure by evaporating these 'chlorine residues' to dryness, and heating the mixture to a dull red heat. On dissolving afterwards in water the iron is left undissolved in the form of ferric oxy-chloride, and the crystals which are obtained from the filtered solution consist of manganous chloride, containing a trace of cobalt. This impurity can be removed by stirring up with the solution a little freshly-precipitated manganous sulphide, and filtering off from the black cobaltous sulphide—

$$Mn S + Co Cl^2 = Mn Cl^2 + Co S.$$

The manganous chloride is deposited from solution in combination with four molecules of water of crystallization—

$$Mn\,Cl^2\,(H^2\,O)^4.$$

Barytic carbonate has no action in the cold on a solution of manganous chloride, but if chlorine be passed into the mixture the manganese is precipitated as manganic oxide or peroxide, by a process analogous to that which occurs in the corresponding treatment of cobaltous chloride.

Manganic perchloride ($Mn^2\,Cl^6$) is no doubt formed by the action of chlorine in the cold on a solution of the manganous chloride, as well as by dissolving manganic oxide in cold hydrochloric acid; but the salt gives off one-third of its chlorine with such extreme readiness that it has never been obtained in the dry state.

**Manganous Sulphide** (Mn S) is precipitated in combination with water by the action of ammonia sulphide on a solution of manganous salt. The sulphide is flesh-coloured. It dissolves with the utmost facility in mineral acids, and even in acetic acid, and can easily be separated from cobaltous sulphide by dilute hydrochloric acid.

Manganous sulphate ($Mn\,S\,O^4$) crystallizes usually with five molecules of water, but at lower temperatures it forms crystals with seven molecules of water. The salt combines with potassic sulphate, forming a double salt which corresponds in its constitution to the potassio ferrous double sulphate.

Manganic sulphate is also known in combination with potassic sulphate. The salt crystallizes in regular octohedral crystals, having the composition—

$$Mn^2\,K^2\,(S\,O^4)^4\,(H^2\,O)^{24}.$$

This salt is isomorphous with alum, and is called manganese alum.

**195.** Potassic manganate ($Mn\,O^4\,K^2$) is a deep green salt, which is readily formed by heating any salt of man-

ganese with an excess of potassic hydrate in contact with the air. The minutest trace of manganese can be discovered by the green colour which is formed by this process. The salt has been crystallized, and found to be isomorphous with potassic sulphate and with potassic chromate.

A solution of potassic manganate decomposes very rapidly when exposed to the air; the addition of a little acid accelerates the change, and causes the green solution to turn purple. This change of colour obtained for the salt the name mineral chameleon. The change of colour is due to the formation of potassic permanganate ($K^2Mn^2O^8$), and is accompanied by the removal of potash and the deposition of manganic peroxide (hydrated). It may be thus represented by an equation—

$$(Mn\,O^4K^2)^3+(H^2O)^2=Mn^2O^8K^2+Mn\,O^2+(H\,K\,O)^4.$$

**Potassic Permanganate** ($Mn^2O^8K^2$) is a salt of a deep purple colour, so intense that very small quantities of manganese can be detected in the wet way by its formation. A mixture of plumbic peroxide and nitric acid, heated with a salt of manganese, gives rise to the formation of a small quantity of permanganic acid. The salt is usually prepared by decomposing potassic manganate by a little nitric acid, and crystallizing the solution. The crystals of potassic permanganate are isomorphous with those of perchlorate.

A solution of potassic permanganate oxidizes organic bodies with extreme facility, and is accordingy used as a disinfecting material.

**196. Zinc** ($Zn=65$; density 7.1 to 7.3). This metal occurs sometimes in combination with sulphur, and is then called blende. A more common ore of zinc is calamine, which is usually a zinc carbonate. The ore is first washed, and the crude zinc oxide obtained in this manner is mixed with coal, and distilled at a bright red heat. Cadmium frequently accompanies zinc. It then comes over in the

beginning of the distillation, and is recognized by the brown 'smoke' (cadmic oxide) formed by the combustion of its vapour. The vapour of zinc burns with a blueish-white flame, depositing white zinc oxide.

Zinc is a very crystalline metal. At a temperature somewhat below 150° it is very soft and ductile, but at about 200° it is exceedingly brittle, and can be powdered in a mortar. It melts at 433°, and distils at a red heat.

Zinc becomes tarnished in moist air by absorbing oxygen. It decomposes steam and carbonic acid at a red heat. With dilute sulphuric or hydrochloric acid it dissolves, giving off hydrogen, and forming zinc sulphate ($Zn S O^4$), or zinc chloride ($Zn Cl^2$). Its action upon nitric acid depends upon the strength of the acid and the temperature at which the action takes place. Nitric oxide, nitrous oxide, nitrogen, or ammonia are formed, according to circumstances. Zinc dissolves in hot caustic potash, giving off hydrogen. It precipitates from acid liquids all the metals of the two first groups. It reduces the ferric salts to ferrous salts, and chromic salts to chromous salts.

Zinc is most used in the alloy with copper, called brass. The proportions of the two metals in brass is subject to considerable variation, the zinc amounting sometimes to no more than 30 per cent. of its weight, sometimes to nearly 50 per cent. The presence of 1 to 1.1 per cent. of iron improves greatly the quality of brass. An alloy of this kind, called sterro-metal, combines, after hammering, an extraordinary amount of tenacity and of elasticity.

**197.** Zinc combines in one proportion only with oxygen, and the oxide shews great analogy with magnesia in its salts, and with a variety of other oxides known to consist of one atom of metal combined with one atom of oxygen. These analogies decide in favour of the formula Zn O. Zinc oxide is most economically prepared by burning the vapour of the

metal as it issues from the neck of the reduction apparatus. It can also be obtained by heating zinc carbonate, or hydrate, or by roasting the sulphide. When obtained by any of these last-named processes it has a yellowish tinge, which does not belong to zinc oxide made by combustion of the metal.

Zinc carbonate ($Zn\ Co^3$) cannot be obtained by the action of an alkaline carbonate on a solution of a salt of zinc, as carbonic acid escapes and a basic salt is precipitated. The normal carbonate occurs, however, in nature crystallized.

Zinc chloride ($Zn\ Cl^2$) is obtained by dissolving the metal in hydrochloric acid, evaporating to dryness, and fusing the residue. During these operations the mass continues liquid, passing from the state of concentrated aqueous solution to that of molten salt. At a red heat the salt evaporates. It is exceedingly soluble in water, and its solution is sold as a disinfecting fluid.

Zinc sulphide is precipitated as a white gelatinous mass by the action of sulphuretted hydrogen on a solution of zinc sulphate, or of the chloride or nitrate. The precipitation is, however, prevented by the presence of a sufficient quantity of free mineral acid, and accordingly is arrested as soon as sulphuretted hydrogen has liberated this proportion of acid from one of the above salts.

Zinc acetate is completely decomposed by sulphuretted hydrogen, even though a large quantity of free acetic acid be present in the solution; and this reaction affords the most convenient means of separating zinc from nickel, as the latter metal is not, or very slightly, precipitated in such a mixture. Zinc sulphide is also precipitated by the action of sulphuretted hydrogen on a solution of zinc oxide in potash.

Zinc sulphate, or white vitriol ($S\ O^4\ Zn$), can be obtained by gently roasting blende. At a high temperature the sulphate

is decomposed, giving off its sulphuric acid, partly as such, partly in the form of a mixture of sulphurous acid and oxygen. The common crystals of the salt are of the composition $S O^4 Zn (H^2 O)^7$. There are also compounds containing a lesser number of molecules of water of crystallization. There is a double salt with potassic sulphate—

$$(S O^4)^2 Zn K^2 (H^2 O)^6.$$

A solution of zinc sulphate dissolves a considerable quantity of metallic zinc, giving off hydrogen and forming basic salts.

**198.** The oxides of the rare metals **Cerium, Lanthanum, Didimium, Yttrium,** and **Glucinum** are to be classed with those of the last-described metals.

Glucina (G O) is contained in the emerald, and has much resemblance to alumina. It dissolves, however, in a solution of ammonia chloride on boiling, and can thus be separated from alumina. It also dissolves in ammonia carbonate. Yttrium, Lanthanum, and Didimium appear to form only protoxides analogous to the cerous oxide (Ce O); but cerium also forms a ceric oxide ($Ce^2 O^3$). The four protoxides form sulphates which combine with potassic sulphate, forming double salts, such as $(S O^4)^2 Ce K^2$, which are nearly insoluble in a saturated solution of potassic sulphate.

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# CHAPTER XXXI.

**199. Barium** (Ba = 137; sp. gr. about 4). This metal is but little known in the free state. It has been obtained by decomposing fused barytic chloride by a galvanic current, or, in combination with mercury, by decomposing a solution of that salt in water containing free hydrochloric acid, while the negative pole was in contact with a drop of mercury.

Sodium or potassium are not able to decompose barytic chloride in an open crucible.

Baryta (Ba O) is a strong base. There is also a higher oxide called barytic peroxide, which is neutral. Baryta occurs frequently in combination with sulphuric acid in the mineral called Heavyspar. Its carbonate, called Witherite, is also found in considerable quantities.

Baryta is most easily prepared by heating barytic nitrate to redness in an earthen crucible. The outer portions of the mass contain silica from the crucible. It is a grey porous mass. Water combines with baryta very energetically, and the hydrate ($Ba\,O^2H^2$) thus formed may be heated to a bright red heat without losing its water. The best way to obtain the hydrate is to heat a mixture of barytic carbonate and coal to a bright red heat for two or three hours, to dissolve in water after cooling, and allow the carbon and residual carbonate to settle. The solution of baryta is intensely alkaline to test-paper. It deposits on evaporation crystals of the composition $Ba\,O^2H^2(H^2O)^8$. These crystals dissolve in about twenty times their weight of cold water, and in a much smaller quantity of boiling water.

The solution is usually called baryta water. It absorbs carbonic acid from the air, depositing barytic carbonate. It precipitates from solutions of their salts all the basic oxides of the preceding groups. It also expels ammonia from its salts.

**Barytic Peroxide** ($Ba\,O^2$) is formed either by heating baryta or its hydrate in oxygen or air. It gives up its second atom of oxygen at a bright red heat. To obtain it in a state of purity its solution in dilute hydrochloric acid should be precipitated by baryta water, and the precipitate deprived of its water by gentle heat.

**Barytic Nitrate** ($Ba\,(N\,O^3)^2$) may be prepared by dissolving finely-powdered barytic carbonate in dilute nitric acid;

but a better process is to add nitric acid to a solution of barytic sulphide—

$$Ba\,S + (N\,O^3\,H)^2 = (N\,O^3)^2\,Ba + H^2S.$$

The salt crystallizes without any water of crystallization, but it generally decrepitates when heated, owing to the presence of water enclosed mechanically by some of the crystals, bursting them asunder by its evaporation.

Barytic nitrate can be precipitated in great part from a saturated solution by the addition of strong nitric acid.

**200. Barytic Carbonate** can be precipitated by an alkaline carbonate from barytic nitrate. The salt is almost perfectly insoluble in water, but an appreciable quantity of it is dissolved by free carbonic acid. Barytic carbonate parts with its carbonic acid at an intense white heat.

Barytic oxalate is insoluble in water but soluble in nitric or hydrochloric acid, and to a very slight extent even in acetic acid.

Barytic cyanide ($(C\,N)^2\,Ba$) dissolves in water with an alkaline reaction. It is decomposed by carbonic acid.

**Barytic Chloride** ($Ba\,Cl^2$) is one of the most commonly used salts of baryta. It is made by dissolving either the carbonate or sulphide in hydrochloric acid. On a large scale it has been prepared by adding manganese residues (impure manganous chloride) to a solution of barytic sulphide, and filtering off the metallic sulphides which are precipitated.

It crystallizes from water in plates which contain two molecules of water ($Cl^2\,Ba\,(H^2O)^2$). It is far more soluble in water than the nitrate, and its saturated solution is precipitated by strong hydrochloric acid. It is insoluble in alcohol if no water be present.

A solution of the salt can be evaporated to dryness and the residue heated without decomposing the salt.

Barytic chlorate ($(Cl\,O^3)^2\,Ba$) crystallizes from water in

beautiful crystals, which are used in the manufacture of green fire.

Iodine decomposes baryta water rapidly, forming a white precipitate of barytic iodate, while barytic iodide remains in the solution—

$$(Ba\,O^2H^2)^6 + I^{12} = (I\,O^3)^2\,Ba + (I^2Ba)^6 + (H^2O)^6.$$

Barytic fluoride ($F^2Ba$) is insoluble in water but soluble in hydrochloric acid.

Barytic sulphide (Ba S) is obtained by heating for several hours an intimate mixture of finely-ground coal and barytic sulphate—

$$S\,O^4\,Ba + C^4 = S\,Ba + (C\,O)^4.$$

The sulphide dissolves readily in hot water; but the solution, if concentrated, deposits on cooling crystals of barytic hydrate, whilst sulph-hydrate remains dissolved and turns yellow by absorption of oxygen—

$$(Ba\,S)^2 + (H^2O)^2 = Ba\,O^2H^2 + Ba\,S^2H^2;$$
$$Ba\,S^2H^2 + O = Ba\,S^2 + H^2O.$$

Cupric oxide decomposes a solution of barytic sulphide, taking up its sulphur, and leaving barytic hydrate in solution.

Barytic sulphide is a strong sulphur base. Its solution dissolves sulphur, forming a barytic pentasulphide $S^5Ba$.

Barytic hyposulphite ($S^2O^3Ba$) is very slightly soluble in water.

Barytic sulphite is a white precipitate, insoluble in water but soluble in nitric or in hydrochloric acid.

Barytic hyposulphate ($S^2O^6Ba$) is most easily prepared by dissolving manganic peroxide in aqueous sulphurous acid, and precipitating the solution by barytic sulphide. The sulphurous and sulphuric acids present in the liquid go down as barium salts, together with the manganous sulphide. The filtered liquid is evaporated and deposits crystals of barytic hyposulphate.

**Barytic Sulphate** ($S O^4 Ba$) is one of the commonest minerals containing this valuable base.

It is perfectly insoluble in water, and its particles are formed so instantaneously when any soluble sulphate comes in contact with a solution containing baryta, that they have no time to arrange themselves into crystals, but go down in the form of an impalpable powder. The salt is not soluble in hydrochloric acid, even on boiling. It dissolves to an exceedingly slight extent in nitric acid, and, moreover, is liable to carry barytic nitrate down with it, when formed in a solution containing nitric acid. In this case the barytic sulphate is found to impart an alkaline reaction to water after it has been heated to redness. Barytic sulphate dissolves to a slight extent in strong sulphuric acid, and is precipitated from that solution by the addition of water. It is not decomposed by heat. Barytic seleniate is very much like the sulphate, but can be distinguished from it by the fact that it dissolves in boiling hydrochloric acid with evolution of chlorine and formation of selenious acid.

Phosphoric acid forms with baryta a normal salt—

$$(P O^4)^2 Ba^3,$$

which is insoluble in water, but which dissolves in nitric or in hydrochloric acid. It also dissolves in phosphoric acid, forming a phosphate of water and baryta $(P O^4)^2 Ba H^4$, tetra-hydrobarytic phosphate.

Phosphorous acid forms an insoluble baryta salt containing

$$(P O^3)^2 Ba^2 H^2 (H^2 O)^n.$$

This salt dissolves in phosphorous acid, forming the salt

$$(P O^3)^2 Ba H^4.$$

Hypo-phosphorous acid forms a soluble and crystallizable baryta salt $(P O^2)^2 Ba H^4$, which is easily obtained by boiling phosphorus in baryta water and crystallizing the solution, after filtering it off from the phosphate and phosphite which are formed at the same time.

Silicic fluoride combines with barytic fluoride, forming a compound represented by the formula $SiF^6Ba$.

Hydrofluosilicic acid precipitates barytic nitrate or chloride, liberating the acid of the salt, and the baryta is almost completely precipitated, in presence of the free hydrochloric or nitric acid. The salt decomposes when heated to redness, giving off silicic fluoride and leaving barytic fluoride.

Boracic acid forms a compound with baryta which is nearly insoluble in water, but which dissolves in various neutral salts; so that boracic acid cannot be carried down completely from a solution in combination with baryta.

Arsenic acid behaves very like phosphoric acid towards baryta. Arsenious acid also forms a neutral salt insoluble in water.

Chromic acid forms a neutral barytic salt ($CrO^4Ba$) of a bright-yellow colour, insoluble in water but soluble in hydrochloric acid. It also forms an acid salt, which is deposited from aqueous solution in red crystals.

**201. Strontium** (Sr = 87.5, sp. gr. 2.58). This metal exhibits in its compounds a close analogy with barium. It occurs as sulphate (called cœlestine), carbonate, and other salts.

Strontic hydrate is less soluble in water than barytic hydrate. The nitrate and chloride are, however, more soluble than the corresponding barium salts.

Strontic nitrate is manufactured for the preparation of red fire. Strontic chloride is somewhat soluble in alcohol, and can thus be separated from barytic chloride.

Strontic sulphate is to a very slight extent soluble in water, and a solution of it precipitates salts of baryta.

Hydrofluosilicic acid does not precipitate a moderately concentrated solution of a salt of strontia. Potassic chromate behaves in like manner.

**202. Calcium** (Ca = 40; sp. gr. 1.56) is reduced in the same manner as barium, and has a reddish tinge approaching to that of copper.

**Lime** (CaO) is one of the commonest and most important of bases. It is most commonly made by heating calcic carbonate. Black marble is the best material for this operation, as the organic matter contained in it reduces the carbonic acid, and thus aids its expulsion. Some varieties of chalk or limestone contain a good deal of silica, which unites with the lime during the operation of burning, and diminishes greatly the value of the product for most purposes. Lime is infusible, but by long exposure to an intense heat it becomes hard from a semi-fusion. It is far less soluble in water than strontia, for it requires 600 or 800 times its weight of cold water for its solution. When such 'lime water' is heated a deposit of lime makes its appearance, for boiling water dissolves only about half as much lime as cold water.

Dry lime (commonly called quicklime) combines with a molecule of water with evolution of great heat, and crumbles into a light powder having the composition $Ca O^2 H^2$. The operation is commonly called 'slaking.'

Calcic hydrate—unlike barytic hydrate—loses its water at a dull red heat.

Water containing calcic hydrate in suspension is usually termed milk of lime.

**203.** Calcic nitrate ($(N O^3)^2 Ca$) is an exceedingly soluble salt, which can with difficulty be obtained in crystals containing $(N O^3)^2 Ca (H^2 O)^4$. Even in the dry state calcic nitrate dissolves in alcohol.

Calcic carbonate ($Ca C O^3$) occurs as calc-spar, and in many other minerals. A variety of calc-spar is found in Iceland in transparent and colourless masses, which are valuable for the construction of polarizing instruments. Calcic carbonate is occasionally found in crystals belonging to a

different system from that to which calc-spar belongs. This mineral is called arragonite.

Calcic carbonate is precipitated by an alkaline carbonate from a solution of calcic chloride or nitrate. The precipitate is gelatinous when first formed, and its particles subsequently arrange themselves more closely together in small crystals, enclosing at the same time some of the liquid which surrounds them.

Calcic carbonate dissolves very slightly in water, but quite sufficiently to diminish the value of the water for many purposes by making it 'hard.'

The presence of free carbonic acid increases greatly the solubility of calcic carbonate, owing to the formation of a hydrocalcic carbonate $(CO^3)^2CaH^2$.

The water from many springs contains this double salt, and, on exposure to the air, deposits calcic carbonate, while half of the carbonic acid evaporates.

Calcic carbonate dissolves on boiling in ammonia chloride, the ammonia carbonate being carried off by the steam as fast as it is formed—

$$CO^3Ca + (NH^4Cl)^2 = Cl^2Ca + CO^3(NH^4)^2.$$

If the products of this reaction be collected and mixed in cold aqueous solution, they decompose one another, and reproduce calcic carbonate and ammonia chloride. Oxalic acid forms with lime a very insoluble salt, which is usually resorted to for the complete precipitation of lime. The oxalate is nearly insoluble in acetic acid, but it dissolves in nitric or in hydrochloric acid. The salt is easily decomposed by heat, its acid breaking up into carbonic oxide, which escapes, and carbonic acid, which remains at first in great part with the lime, but is in its turn expelled by stronger heat.

Calcic chloride ($Cl^2Ca$) is a waste product formed in several manufactures, and is of value for drying gases, as well as for the artificial production of cold. It undergoes

a partial decomposition during the process of driving off water from the moist salt, but the dry mass, although basic, does not absorb carbonic acid. Calcic chloride crystallizes from a very concentrated aqueous solution, in combination with six molecules of water, of which four are easily expelled by gentle heat. These crystals are used for freezing mixtures. The dry chloride evolves heat on combining with water. Calcic chloride dissolves readily in alcohol.

**Chloride of Lime,** or bleaching-powder, are names given to a mixture containing calcic hypochlorite, and valuable only in proportion to the quantity of this salt which it contains. It is prepared by passing chlorine over trays in which slaked lime is spread out. When chloride of lime is exposed to the air, the calcic hypochlorite contained in the substance is decomposed by carbonic acid, with liberation of hypochlorous acid, which is gradually given off. The salt is decomposed by heat into calcic chloride and chlorate—

$$(Ca\,Cl^2O^2)^3 = (Cl\,O^3)^2\,Ca + (Cl^2Ca)^2.$$

Calcic fluoride, or fluorspar ($F^2Ca$), is found in beautiful cubical crystals, sometimes green, sometimes purple, while other specimens are amber-coloured. It is very slightly soluble in water, but dissolves in hydrochloric acid.

Calcic sulphide (S Ca) can be obtained by the action of sulphuretted hydrogen on red-hot lime. It is not soluble in water, but is gradually decomposed by water, especially with the aid of heat, into calcic hydrate and calcic sulph-hydrate, the latter compound dissolving while the former remains in great part undissolved—

$$(Ca\,S)^2 + (H^2O)^2 = Ca\,O^2H^2 + Ca\,S^2H^2.$$

Milk of lime dissolves large quantities of flowers of sulphur when the two substances are boiled together. The yellow solution thus obtained consists of a mixture of calcic penta-sulphide and calcic hyposulphite—

$$(Ca\,O^2H^2)^3 + S^{12} = (Ca\,S^5)^2 + S^2O^3Ca + (H^2O)^2.$$

At a red heat calcic sulphate is formed, and a lower calcic sulphide.

Calcic sulphite ($So^3Ca$) is an insoluble salt in water. It dissolves, however, in sulphurous acid, with formation, no doubt of a hydrocalcic sulphite.

**204. Calcic Sulphate** is found crystallized without water, and is then called 'anhydrite.' It occurs more commonly in combination with two molecules of water—

$$S\,O^4Ca\,(H^2O)^2,$$

and is then called 'gypsum' or plaster of Paris. This compound loses its water of crystallization at about 130°, and the powder of the salt, dried at this temperature, solidifies to a coherent mass by resuming its water of crystallization, when mixed with a suitable quantity of water. If it has been exposed to a temperature of nearly 200° it solidifies much more slowly when moistened. The salt requires about 400 parts of water for its solution, and is accordingly precipitated by the action of a soluble sulphate upon calcic chloride, if less than this proportion of water be present. A saturated aqueous solution of calcic sulphate forms an immediate precipitate when mixed with a solution of a salt of barium, and it forms more slowly a smaller precipitate when mixed with a soluble salt of strontium.

Calcic sulphate is insoluble in alcohol and in water containing a large quantity of alcohol.

**Calcic Phosphate** is the chief constituent of bone-ash. It can be obtained by precipitation, but has then generally some hydrogen in place of a part of its calcium. Its formula is $(Po^4)^2\,Ca^3$. The salt dissolves in nitric or hydrochloric acid. It is decomposed by sulphuric acid, with formation of calcic sulphate and the soluble tetrahydro-calcic phosphate $(Po^4)^2\,Ca\,H^4$.

A mixture obtained in this manner is largely manufactured as a manure, and goes by the name of superphosphate of

lime. Acetic acid dissolves calcic phosphate easily if the salt be first dissolved in hydrochloric acid and precipitated as a gelatinous mass by ammonia.

Calcic silicate occurs in crystals having the composition $SiO^3Ca$. The mineral is called taburlar spar.

Calcic silicate is probably the compound which is formed when hydraulic mortar becomes hard. A mixture of clay and lime is ground up very finely together for the preparation of this material, and the action of water upon it induces the combination to which the hardening is due.

Building mortar is a fine mixture of slaked lime with sand, and its hardening is attributed to the gradual absorption of carbonic acid by the lime. A calcic silicate is, however, doubtless formed on the surface of the granules of sand.

An artificial stone of great strength is manufactured by precipitating calcic chloride gradually by a solution of sodic silicate, in presence of a large quantity of sand. Calcic silicate is at first formed in a gelatinous state, and gradually contracts on drying, and binds the granules of sand together very firmly.

**205. Magnesium** (Mg = 24). This metal is analogous to the alkaline earths in some of its properties, but is more closely connected with zinc and cadmium. It is prepared by the action of sodium on magnesic chloride, and is purified by distillation. It is a white metal, and does not tarnish in dry air. It can be pressed into wire, and a piece of its wire when kindled in a flame burns with considerable brilliancy, forming a white powder of magnesia (Mg O).

**Magnesia** is widely diffused through the mineral kingdom. The sea-water owes its bitter taste to the presence of a salt of magnesia; and magnesic sulphate is found occasionally in mineral waters. The earth itself is usually made by calcining magnesic carbonate. It is nearly insoluble in water, but when put upon faintly-reddened moist litmus-paper it

imparts a blue colour to it. Magnesic hydrate is precipitated as a gelatinous mass by potash, and even by ammonia, from the sulphate or nitrate, &c. It is also precipitated by baryta. Magnesia dissolves readily in ammoniacal salts, and for this reason ammonia gives no precipitate in the solution of a salt of magnesia, containing originally much free acid or salt of ammonia.

Magnesia becomes pink when moistened with a solution of cobaltous nitrate and heated before the blow-pipe.

Magnesic nitrate ($(NO^3)^2Mg$) is an exceedingly soluble salt which deliquesces in moist air. It crystallizes from a concentrated solution with six molecules of water, and is soluble in alcohol.

**Magnesic Carbonate** occurs frequently with calcic carbonate in one crystal. It can be precipitated in combination with water from a magnesia salt by double decomposition, but is very liable to lose some of its carbonic acid, taking up water instead. The salt is easily deprived of its carbonic acid by calcination. It dissolves in ammonia carbonate, forming a double carbonate, which crystallizes out from the solution on standing. Magnesic carbonate dissolves in carbonic acid water to a far greater extent than calcic carbonate, and a solution of magnesic hydrocarbonate is used in medicine under the name of "fluid magnesia." The solution has an alkaline reaction. The solution is readily decomposed by boiling, and even by exposure to the air, carbonic acid going off.

Magnesic oxalate ($C^2O^4Mg$) is very slightly soluble in water but readily soluble in ammonia salts, and lime can accordingly be separated completely from magnesia by means of oxalic acid in such a solution.

Magnesic chloride ($Cl^2Mg$) cannot be obtained in a pure state by evaporation of its aqueous solution, for hydrochloric acid passes off with the water and a basic salt is left.

It is now prepared for the manufacture of magnesium by evaporating the very concentrated solution in a stream of hydrochloric acid gas. The chloride melts readily. It is exceedingly soluble in water.

Magnesic hydrate is dissolved in considerable quantity by water through which a stream of sulphuretted hydrogen is passed, and forms the magnesic sulph-hydrate $Mg\,S^2\,H^2$.

Magnesic sulphate ($S\,O^4\,Mg$), commonly called Epsom salts, occurs usually in crystals containing seven molecules of water of crystallization, which are isomorphous with the corresponding crystals of zinc sulphate. One of these molecules of water is supposed to be replaced by potassic sulphate in the double salt $(S\,O^4)^2\,Mg\,K^2\,(H^2\,O)^6$.

Magnesic sulphate dissolves in about three times its weight of cold water, and the solution has the bitter taste which belongs to all soluble salts of the earth. It is not soluble in alcohol. A bright red heat decomposes magnesic sulphate completely.

One of the most important magnesian salts is an ammoniomagnesic phosphate, which has a composition represented by the formula $P\,O^4\,Mg\,N\,H^4\,(H^2\,O)^6$. This salt is very slightly soluble in water, and insoluble in water containing free ammonia. It is, however, deposited very slowly from a dilute solution in which its constituents are brought together. It dissolves readily in acids. At a red heat it loses all its water and ammonia, leaving so-called magnesic pyrophosphate, properly called dimagnesic diphosphate—

$$(P\,O^4\,Mg\,N\,H^4\,(H^2\,O)^6)^2 = P^2\,O^7\,Mg^2 + (N\,H^3)^2 + (H^2\,O)^{13}.$$

# CHAPTER XXXII.

**206. Potassium** (K = 39 ; sp. gr. 0.86 ; melting-point, 62.5°). This remarkable body was first obtained by Davy by the action of a strong galvanic current on potassic hydrate moistened by a small quantity of water. It has since been prepared by the action of finely-divided metallic iron on potassic hydrate at a white heat. Also by heating potash with charcoal to a white heat.

It is rapidly oxidized by the air even at low temperatures, and must therefore be collected and kept out of contact with the air. At the ordinary temperature potassium is a soft metal of a consistency somewhat similar to soft wax. At a red heat it can be distilled. It decomposes water with great violence, and evolves at the same time sufficient heat to kindle the hydrogen which is given off.

In air or oxygen it burns with formation of a white smoke, which consists of potassic tetroxide ($K^2O^4$).

When heated in an atmosphere of carbonic acid it decomposes the gas with a bright glowing light, and a deposit of carbon is left in the place which was occupied by the potassium. It absorbs carbonic oxide; and when potassium is reduced by the action of charcoal, a considerable proportion of the product is lost by combining with the carbonic oxide simultaneously formed.

Potassium forms a very strong base called potash, consisting of two atoms of the metal united with one atom of potassium ($K^2O$). The anhydrous potash is obtained by heating potassic hydrate with metallic potassium—

$$HKO + K = K^2O + H.$$

**207. Potassic Hydrate,** or 'caustic potash,' as it is usually called, is commonly prepared by boiling a solution of potassic carbonate with milk of lime. The potassic carbonate is dissolved in about twelve times its weight of water, and heated to the boiling-point in an iron pan. Quicklime (about two-thirds of the weight of the carbonate) is slaked in four times its weight of hot water, and this lime-milk added little by little to the boiling solution of potassic carbonate. A precipitate of calcic carbonate is formed, which should be allowed to settle while the pot is kept carefully covered—

$$Co^3K^2 + Ca\,O^2H^2 = (H\,K\,O)^2 + C\,O^3\,Ca.$$

The clear liquid should be siphoned off and evaporated in a metallic vessel without contact with the air.

The residue can be fused, and cast into sticks or any other convenient form. The fusion should take place in a silver vessel.

Potassic hydrate made in this way generally contains a good many impurities—viz. carbonic, sulphuric, and phosphoric acids, and chlorine, besides silica or alumina. Most of these are left behind as potassium salts when the potash is dissolved in alcohol. The impurities of the product are mostly due to the impure nature of the materials employed, but neither lime nor potassic carbonate are easily to be obtained in the pure state, and processes have accordingly been devised for preparing potash from materials which are easily obtained pure. One such process is the precipitation of a solution of potassic sulphate by baryta water—

$$S\,O^4K^2 + Ba\,O^2H^2 = S\,O^4\,Ba + (H\,K\,O)^2.$$

Another is to fuse potassic nitrate in a copper crucible until no further evolution of gas takes place, and then to continue the heating in presence of some finely-divided metallic copper. The copper reduces nitrogen from a small quantity of nitrite, which cannot easily be decomposed by heat alone.

Potash dissolves animal membranes rapidly, and has thus

acquired the title of 'caustic.' It also attacks glass, more especially the softer kinds of glass, and when kept in solution in a glass bottle it is accordingly liable to contain silica.

It liberates baryta, lime, or magnesia from solutions of their salts, and expels ammonia readily.

**208. Potassic Nitrate,** or saltpetre ($NO^3K$), is formed by the decomposition of nitrogenized animal matter, in contact with clay or other minerals capable of yielding potash, and can be obtained in considerable quantities by washing the earth excavated from the neighbourhood of houses which have been long inhabited, and evaporating the filtered solution till it crystallizes on cooling. It is not unfrequently prepared from sodic nitrate, by crystallizing a mixture of that salt with potassic chloride, the potassic nitrate being less soluble than the sodic salt—

$$NO^3Na + ClK = NO^3K + ClNa.$$

It is usually contaminated with common salt, from which it can be purified by crystallization.

Nitre is chiefly used for the manufacture of gunpowder—a mechanical mixture of charcoal, sulphur, and nitre. The proportions of these materials usually approach that represented by the formula $(NO^3K)^2 + S + C^3$; and the combustion of the carbon forming $(CO^2)^3$, leaves sulphur to combine with the potassium ($K^2S$), while nitrogen is liberated. Some secondary products always accompanying these.

Potassic nitrite ($KNO^2$) is prepared by cautiously heating the nitrate and purifying by crystallization.

Potassic nitride is obtained by heating potassium in a stream of ammonia gas. The first reaction consists in potassium displacing one atom of hydrogen in the ammonia—

$$NH^3 + K = NH^2K + H;$$

but when this potassic amide is heated, it decomposes into ammonia and potassic nitride—

$$(NH^2K)^3 = NK^3 + (NH^3)^2.$$

Both compounds are immediately decomposed by water into ammonia and potassic hydrate.

**209. Potassic Carbonate** ($CO^3K^2$) is the salt which was originally called potash, from the circumstance of its being contained in the ashes left on the combustion of wood. It is most commonly made by dissolving the ashes of land plants in a small quantity of water, insufficient for the solution of the other constituents of the ash, and evaporating the solution to dryness. A subsequent calcination serves to destroy the organic matter which frequently accompanies the crude potash.

It usually contains sulphuric and phosphoric acid, and a chloride, besides silica. For laboratory use a much purer carbonate can be obtained by fusing hydropotassic tartrate in a platinum crucible, and dissolving out the carbonate which is formed, from the charcoal which accompanies it.

Potassic carbonate is alkaline to test-paper. It absorbs water from moist air, and if left long enough forms a thick oily liquid. It is not soluble in alcohol.

Hydropotassic carbonate ($CO^3KH$) crystallizes out from a solution of potassic carbonate which is placed in contact with carbonic acid. The salt is decomposed by ebullition of its aqueous solution.

Potassic oxalate ($C^2O^4K^2$) is a neutral salt obtained by neutralizing sorrel salt by potassic carbonate.

Hydropotassic oxalate ($C^2O^4KH$) is found in the juice of sorrel, and imparts to that plant its acid taste. When oxalic acid is added to a concentrated solution of this salt, a compound of it with oxalic acid is precipitated, having a composition represented by this formula—

$$(C^2O^4KH)\,(C^2O^4H^2)\,(H^2O)^2.$$

This salt is called trihydropotassic dioxalate.

**210.** Potassic cyanide ($CNK$) can be obtained by fusing potassic ferrocyanide in a closed crucible at a bright red heat,

and allowing the iron and carbon to settle at the bottom of the liquid mass. When cold, the crucible must be broken, and the black portion of its contents separated from the white potassic cyanide. The salt is frequently prepared, together with some potassic cyanate, by fusing dry potassic ferrocyanide with about one-third its weight of potassic carbonate. The first reaction is no doubt the formation of ferrous carbonate, but this is speedily reduced to the metallic state, forming potassic cyanate—

$$(Cy)^6\,Fe\,K^4 + C\,O^3\,K^2 = (C\,N\,K)^5 + C\,N\,K\,O + Fe + C\,O^2.$$

The salt can be purified by crystallization from spirits of wine, and is then obtained in cubes.

Potassic cyanide is formed by heating potassic carbonate with nitrogenized animal matter. It is also found in the gases which rise from the hottest part of the blast furnace.

Its aqueous solution is intensely alkaline, and even carbonic acid decomposes it, liberating prussic acid. At high temperatures potassic cyanide is a powerful reducing agent, taking up an atom of oxygen from ferrous oxide or lead oxide, and forming potassic cyanate (C N K O). This salt can be obtained by fusing potassic cyanide with about three and a half times its weight of litharge, and dissolving the product in hot spirits of wine, which deposits potassic cyanate on cooling. Potassic cyanate is decomposed by moist air, ammonia escaping, and hydro-potassic carbonate remaining behind; $C\,O\,K\,N + (H^2O)^2 = C\,O^3\,H\,K + N\,H^3$.

Potassic cyanide also combines readily with sulphur, either while dissolved in water or when fused with sulphur, forming potassic sulphocyanate (C N K S); which is an exceedingly soluble salt in water, and is not decomposed by contact with it like the cyanate.

**211. Potassic Chloride** (Cl K) is prepared from the mother liquor of sea-water, and a considerable quantity of it has been found near Magdeburg mixed with sodic chloride.

It crystallizes in cubes, containing no water of crystallization. At high temperatures the salt is readily volatilized.

Its double salt with platinic chloride ($Pt\,Cl^6K^2$) is very slightly soluble in water and insoluble in alcohol. When sulphuric acid is present in a mixture containing potash, platinic chloride forms a precipitate containing both sulphate and chloride.

**Potassic Chlorate** ($K\,Cl\,O^3$) is a salt largely manufactured for the preparation of lucifer matches. It can be obtained by heating the mixture of potassic chloride and hypochlorite, which is formed by the action of chlorine on caustic potash. The hypochlorite breaks up into potassic chloride and potassic chlorate—

$$(Cl\,K\,O)^3 = (Cl\,K)^2 + Cl\,O^3K.$$

It is usually prepared by adding potassic chloride to a mixture of calcic chloride and calcic chlorate, and evaporating to crystallization—

$$(Cl\,O^3)^2\,Ca + (Cl\,K)^2 = (Cl\,O^3\,K)^2 + Cl^2\,Ca.$$

It crystallizes in anhydrous plates.

On decomposing the salt by heat a portion of it takes up oxygen, and becomes converted into potassic perchlorate ($Cl\,O^4K$), which requires a higher temperature for its decomposition. Potassic perchlorate is one of the least soluble of potash salts in water, and its solubility is still less in presence of alcohol.

Bromine decomposes potash rapidly, forming at once a mixture of potassic bromide and potassic bromate—

$$Br^6 + (H\,K\,O)^6 = (Br\,K)^5 + (Br\,O^3K) + (H^2O)^3.$$

Iodine acts in a similar manner; and if strong potash be used potassic iodate is speedily deposited. In the manufacture of **Potassic Iodide** it is customary to evaporate to dryness a mixture of the two salts, and to decompose the potassic iodate by heat.

Potassic iodide crystallizes in anhydrous cubes, which are

very apt to become tinged by free iodine, if exposed to air containing any free acid; for hydriodic acid, which is at first liberated from them, is rapidly oxidized by the air. The commercial salt sometimes contains a little potassic iodate.

Potassic fluoride (F K) is a very soluble salt which crystallizes in cubes. Its solution attacks glass.

Hydropotassic fluoride ($F^2KH$) is obtained by crystallizing a mixture of hydrofluoric acid and potassic fluoride.

Potassic fluoboride ($BF^4K$) is a soluble salt which crystallizes from water. It gives off boric fluoride at a red heat, leaving potassic fluoride.

Potassic fluosilicate ($SiF^6K^2$) is precipitated by the action of hydrofluosilicic acid on a salt of potash, such as nitrate chloride, &c. It is an opalescent semi-transparent precipitate not quite insoluble in water.

**212. Potassic Sulphide** ($SK^2$) is formed by the action of hydrogen or carbon upon potassic sulphate at a red heat. An aqueous solution of it is obtained by dividing a solution of potash into two equal parts, saturating one of them by sulphuretted hydrogen, boiling to expel the excess of sulphuretted hydrogen, and then mixing with the remaining half of the potash. The solution is colourless and strongly alkaline. Acids decompose it with evolution of sulphuretted hydrogen, and without any deposition of sulphur. The solution readily dissolves sulphur to the extent of four additional atoms, forming potassic pentasulphide ($S^5K^2$). Even one atom of sulphur added to the sulphide gives it a yellow colour, and causes a deposition of sulphur when an acid is added to the solution—

$$S^2K^2 + (HCl)^2 = SH^2 + (ClK)^2 + S.$$

Carbonic acid decomposes potassic sulphide, hence its 'hepatic' smell.

Potassic sulph-hydrate (SKH) is obtained by saturating potash by sulphuretted hydrogen, and boiling away the

excess of the gas. It crystallizes in colourless crystals. Its solution, as well as that of potassic sulphide, absorbs oxygen from the air, forming potassic hyposulphite.

Potassic sulphite ($SO^3K^2$) is obtained by decomposing potassic carbonate by sulphurous acid.

Hydropotassic sulphite ($SO^3KH$) is formed by the action of the last-named salt on sulphurous acid in presence of water. It is precipitated from its solution by alcohol.

**213. Potassic Sulphate** ($SO^4K^2$) is deposited from water in hard crystals, which contain mechanically-enclosed water, and usually decrepitate when heated, but no water of crystallization. It is not decomposed by heat. It dissolves in about ten times its weight of cold water, but the addition of hydrochloric acid increases its solubility by forming potassic chloride and hydropotassic sulphate, which is more soluble than potassic sulphate itself—

$$SO^4K^2 + HCl = SO^4KH + ClK.$$

Potassic disulphate ($S^2O^7K^2$) crystallizes out from a solution of potassic sulphate in two molecules of hydric sulphate. It gives off sulphuric acid when strongly heated.

Hydropotassic sulphate ($SO^4KH$) is obtained in the preparation of nitric acid in the laboratory. The salt dissolves in about half its weight of boiling water, but when the solution is crystallized some crystals of neutral potassic sulphate are deposited among those of the double salt, and by successive crystallizations the whole salt may be decomposed into hydrated acid and neutral salt.

**214.** The normal **Potassic Phosphate** ($PO^4K^3$) is obtained by fusing phosphoric acid with potassic carbonate. It has an alkaline reaction to test-paper. The hydro-di-potassic phosphate ($Po^4K^2H$) is a nearly neutral salt; it has not, however, been obtained in crystals. The di-hydropotassic phosphate ($Po^4KH^2$) is acid to test-paper.

Arsenic acid forms three salts similar to these.

Antimonic acid forms a soluble compound with two atoms of potassium, and probably one of hydrogen also, which is obtained by fusing the acid with potassic hydrate; and also a salt of the composition $Sb\,O^4K\,H^2(H^2O)^2$.

Chromic acid forms two crystallizable salts with potash, viz. the neutral potassic chromate ($Cr\,O^4K^2$), which is obtained in yellow crystals isomorphous with potassic sulphate; and potassic dichromate ($Cr^2\,O^7K^2$), the common commercial salt, frequently called from its colour, red chromate. It is made by fusing chrome-iron-ore with nitre. The crystals are anhydrous.

Potassic permanganate ($Mn^2O^8K^2$) is obtained by decomposing potassic manganate by water, pouring off from the precipitate of manganic peroxide, and evaporating to crystallization. It is obtained in purple needles, isomorphous with potassic perchlorate, and capable of crystallizing with that salt in all proportions.

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# CHAPTER XXXIII.

**215. Sodium** (Na=23; sp. gr. 0.97; melting-point, 98°). This metal is reduced by the action of charcoal at a white heat on sodic carbonate. It distils over in the carbonic oxide which is simultaneously formed, and, unlike potassium, it does not combine with any of that gas. The preparation of sodium is much easier than that of potassium, and the metal is now manufactured in considerable quantities for the reduction of aluminium and magnesium.

Sodium decomposes water, when thrown upon its surface, with less intensity than potassium does, and the heat evolved is not sufficient to kindle the hydrogen which is given off.

Soda ($Na^2O$) can be obtained by the action of sodium upon fused sodic hydrate.

**Sodic Hydrate** is now prepared on a large scale by the action of milk of lime on a solution of carbonate of lime, and the caustic liquid deposits at a certain concentration all the foreign salts present in a solid state, so that they can be skimmed or strained off from the liquid soda. Hydrate of soda dissolves readily in water with evolution of heat, forming an intensely caustic liquid.

According to Dalton a solution of soda of 1.56 density contains 41.2 per cent. of anhydrous soda ($Na^2O$). At 1.36 it contains 26 per cent.; at 1.18 it contains 13 per cent.

Sodic nitrate, or Chili saltpetre ($NO^3Na$), is obtained chiefly from dry districts of Chili, where it is present in large quantities on the surface of the soil. It is not used for the manufacture of gunpowder in consequence of being deliquescent in moist air. It is also more soluble in water than the potash salt.

**216. Sodic Carbonate** ($CO^3Na^2$) is popularly called 'soda.' It used to be made from the ashes of sea-weeds. But the chief manufacture of soda is now by a process originally proposed by Leblanc, of which the introduction has constituted an era in the history of chemical manufactures.

The process consists of two stages: first, the preparation of sodic sulphate from common salt; secondly, the reduction of this sulphate ($Na^2SO^4$) to sodic sulphide ($Na^2S$) in presence of calcic carbonate. These compounds exchange metals, forming calcic sulphide and sodic carbonate.

The first operation is performed in large cast-iron pans about 12 inches deep in the centre and 9 feet diameter, each pan being the segment of a sphere. Each pan is roofed over by a similar cast-iron vessel with openings. A charge of 5 or 6 cwt. of salt is thrown into one of these pans, and about an equal weight of sulphuric acid, of the density

1.7, run in upon it. The bottom of the pan is heated by a fire until the decomposition of the salt by the acid is rather more than half complete—

$$SO^4H^2 + ClNa = SO^4NaH + HCl.$$

The hydrochloric acid which goes off is conducted to the bottom of a vertical flue full of pieces of coke, and while it rises upwards through this flue it meets water which is being poured in at the top, and which is trickling down over the coke. In this manner the acid is completely condensed by water. When the action in the pan becomes sluggish, the charge is scraped out of it and exposed to a higher temperature in a chamber of fire-brick, of which the bottom is heated by the flues from a furnace. Hydrosodic sulphate, which was present in the charge, then decomposes the remainder of the salt; $SO^4NaH + ClNa = SO^4Na^2 + ClH$.

The sodic sulphate is then ground up with about an equal weight of chalk and half its weight (or rather more) of coal, and the mixture well melted by the flames of a reverberatory furnace, and after stirring is raked out to cool. It is then called black ball or black ash. The sodic carbonate has to be dissolved out from it as speedily as possible and crystallized, calcic sulphide remaining behind undissolved. Caustic soda is usually present; and this is separated from the crystals of the carbonate and evaporated to dryness for use in the caustic state, after the sodic sulphide and cyanide with which it is contaminated have been oxidised by fusion with sodic nitrate.

The common crystals of sodic carbonate contain ten molecules of water of crystallization ($CO^3Na^2(H^2O)^{10}$); part of which evaporates in dry air, while the crystals crumble to powder, or effloresce, as it is called. Commercial sodic carbonate commonly contains sulphuric acid and chlorine; occasionally hyposulphurous acid, sulphide, and cyanide. The best way to obtain pure sodic carbonate is to wash hydro-

sodic carbonate, and decompose it by a dull red heat, driving off carbonic acid and water. Sodic carbonate has an unpleasant, bitter, and alkaline taste, and is strongly alkaline to test-paper. It is not soluble in alcohol.

**Hydrosodic Carbonate** ($C O^3 Na H$) is usually made by exposing crystals of the carbonate to carbonic acid gas. It is far less soluble in water than the simple salt, and is decomposed gradually by boiling water, carbonic acid escaping.

A beautiful double carbonate containing potash and soda is easily obtained by dissolving the salts together in approximatively atomic proportions. The crystals consist of

$$C O^3 K Na (H^2 O)^6.$$

**217. Sodic Chloride**, or common salt ($Cl Na$), is the most plentiful of the soluble salts of soda. It constitutes nearly three per cent. of the weight of sea-water, and in some climates is obtained by the spontaneous evaporation of sea-water in shallow enclosures by the sea-side. The crystals thus obtained are usually distinguished by the name 'bay salt' from those prepared from subterranean sources. The evaporation is carried on until the remaining liquid has acquired a density of about 1.24. This mother liquid deposits sodic sulphate if artificially cooled to about $-17°C$, and by further evaporation can then be made to deposit nearly all the sodic chloride left in it while still hot.

The remaining liquid deposits on cooling crystals of a double chloride, containing potassium and magnesium; and from this double salt the magnesic chloride can be washed out by cold water, with a part of the potassic chloride, leaving the remainder of the potassic chloride in a pure state. This series of operations has been invented by M. Balard, aided in some particulars by M. Merle.

Sodic chloride is found in several parts of the world in large deposits in the earth, as so-called rock-salt, and in some localities in a state of great purity.

It crystallizes in cubes which contain no water of crystallization. A solution of salt saturated at the common atmospheric temperature (15°C) has a specific gravity of 1.204, and contains about 26.5 parts of salt. The addition of alcohol or of strong hydrochloric acid throws down some of the salt. Salt is volatilized to a considerable extent at a strong red heat, and in presence of moisture—silica or alumina decomposes it, with evolution of hydrochloric acid.

It forms with platinic chloride a double salt ($Pt\,Cl^6\,Na^2$), which is soluble in alcohol, and soda is thus separated from potash.

Sodic chlorate cannot be separated from sodic chloride by crystallization, and for this reason potash is preferred as a base for holding chloric acid.

Salts of soda are not precipitated by hydrofluosilicic acid. The sodic sulphides are obtained by processes similar to those described for the potassic sulphides. Sodic hyposulphite ($S^2\,O^3\,Na^2$) is a salt considerably used by photographers for fixing, i. e. dissolving off the superfluous silver iodide from the developed plates. It can be obtained by dissolving sulphur in caustic soda by the aid of heat, and into the mixture of sodic hyposulphite and sulphide thus obtained leading sulphurous acid until the sulphide is decomposed. The salt usually crystallizes with five molecules of water—

$$S^2\,O^3\,Na^2\,(H^2\,O)^5.$$

**218. Sodic Sulphate,** or glaubers salt, is usually made by the action of sulphuric acid on common salt. It is most commonly met with in efflorescent crystals consisting of $S\,O^4\,Na^2\,(H^2\,O)^{10}$. It can also be obtained with $(H^2\,O)^7$, and even in anhydrous crystals.

The solubility of sodic sulphate in water increases with rise of temperature up to 33°C, but a solution saturated at that temperature deposits some of its salt when the temperature is raised.

A solution of the salt, saturated at a high temperature and allowed to cool in a closed vessel, retains a larger quantity of salt in solution than it would take up at this lower temperature, and it is then called super-saturated. When such a solution is poured out of t e vessel in whic ı it had cooled down it suddenly deposits a quantity of crystals with evolution of heat.

Sodic sulphate is not decomposed by heat.

Sodic disulphate ($S^2\,O^7\,Na^2$) is formed by heating the hydrosodic sulphate at a dull red heat, until fumes of sulphuric acid begin to make their appearance. Two molecules of the double salt eliminate one molecule of water, and form one molecule of the acid sulphate—

$$(S\,O^4\,Na\,H)^2 = S^2\,O^7\,Na^2 + H^2\,O.$$

At a strong red heat the salt is decomposed, leaving neutral sodic sulphate.

The double sulphate containing sodium and hydrogen ($H\,Na\,S\,O^4$) has considerable resemblance to the corresponding double salt containing potassium, and is decomposed with even greater readiness, by water or alcohol, into hydrated sulphuric acid and the neutral sulphate.

**219. Sodic Phosphate** occurs commonly in the form of the double salt with hydrogen, containing one atom of hydrogen and two of sodium. The crystals of this hydro-disodic phosphate contain 12 molecules of water of crystallization—

$$P\,O^4\,Na^2\,H\,(H^2\,O)^{12}.$$

This salt is not unfrequently called rhombic phosphate, from the circumstance of its occurring in rhombic prisms. It is obtained by adding sodic carbonate to a solution of phosphoric acid or of tetra-hydrocalcic phosphate. The salt is slightly alkaline to test-paper. The crystals dissolve in about four times their weight of cold water, or half that quantity of boiling water. When the salt is heated to redness it loses all its hydrogen as water, leaving an acid phosphate of the composition $P^2\,O^7\,Na^4$, which is considerably less soluble in water

than the rhombic salt. This salt is commonly called pyro-phosphate, but its systematic name is tetra-sodic diphosphate. Nitric acid decomposes common hydro-disodic phosphate, forming sodic nitrate, and replacing one atom of sodium in the salt by one of hydrogen. The addition of alcohol to such a mixture precipitates a salt acid in its reactions—

$$P O^4 Na^2 H + N O^3 H = N O^3 Na + P O^4 Na H^2.$$

Caustic soda added to a solution of the rhombic phosphate decomposes it by removing its hydrogen, and replacing it by an atom of sodium—

$$P O^4 Na^2 H + H O Na = P O^4 Na^3 + H^2 O.$$

This phosphate of soda is strongly alkaline, and is decomposed even by carbonic acid, with reproduction of the rhombic salt.

When sodic phosphate is mixed with a molecule of ammonia chloride in presence of little water, a triple salt called microcosmic salt is formed, containing sodium, ammonium, and basic hydrogen—

$$P O^4 Na^2 H + Cl N H^4 = P O^4 Na (N H^4) H + Cl Na.$$

This salt leaves at a red heat a residue called sodic meta-phosphate—$P O^4 Na N H^4 H - N H^3 - H^2 O = P O^3 Na$.

Boracic acid forms a great many double salts with soda and water. Borax is the name given to the common salt $B^4 O^7 Na^2 (H^2 O)^{10}$, which is made by dissolving boracic acid in sodic carbonate. Borax is alkaline to test-paper.

**220.** Sodic disilicate is now manufactured for the preparation of artificial stone, and also as a constituent of some kinds of soap. Caustic soda is heated with flint stones in a high-pressure boiler, which is revolving on a horizontal axis, so that the contents are continually agitated. It is usually sold at a density of about 1.5. When made by fusion of silica with sodic carbonate it contains acid and base in proportions corresponding to the compound $Si O^3 Na^2$. The compound has been obtained in crystals from an aqueous solution. A

solution of this salt dissolves silica, forming a solution which contains silica and soda in proportions corresponding nearly to a tetrasilicate of soda ($Si^4 O^9 Na^2$).

Double silicates, containing soda and lime, are the chief constituents of common window and bottle glass. The presence of the calcic silicate, or of some such salt, is needed to prevent the alkaline silicate from dissolving in water.

**Glasses** made for different purposes present some differences of composition. Thus, the hard glass used for operations in which a very high temperature is resorted to, consists of potassic silicate combined with calcic silicate. Glass for lustres, or for optical instruments, in which considerable dispersive power is needed, is made of an alkaline silicate combined with plumbic silicate, and is usually distinguished by the name 'flint glass.' The composition of very few kinds of glass agrees with any exact formula, as they are to some extent mixtures in various proportions of definite compounds; but the following formulæ represent very nearly a couple of the more important varieties, which may serve as samples—

$(Si O^2)^4 (Ca O) (Na^2 O)$, French window glass.

$(Si O^2)^6 (Pb O) (K^2 O)$, English flint glass.

Aluminium partially replaces sodium in many of our common kinds of glass, and oxide of iron is usually present.

For the common kinds of glass the materials are melted together in open pots made of very infusible clay; but flint glass is melted in pots which open only to the air of the room in which the furnace is contained, so that no ashes or products of imperfect combustion can reach the glass. This precaution is necessary to protect the flint glass from the blackening which it would undergo by contact with carbonic oxide or smoke.

When the glass has been moulded into the proper shape it has to undergo a process of baking, called annealing, at a

temperature intermediate between that of the glass pot, and that of the air in which the glass vessel is to be kept. The effect of this process is to allow the particles of the viscid material time to contract gradually and uniformly, to the volume corresponding to lower temperatures. Suddenly-cooled glass is liable to break into fragments, or even into powder, when its surface is even scratched; and imperfectly-annealed glass is liable to break, far more easily than glass which has been well annealed. Some kinds of glass are liable to become opaque like earthenware if long exposed to a high temperature. This process of devitrification is attributed to a crystallization of components of the glass. The material thus formed is called Reaumur's porcelain.

Glass is coloured by various metallic oxides which are dissolved in it. Thus, the green colour of bottle glass is due to ferrous oxide, and ferric oxide imparts a reddish yellow colour. Green colours are given by cupric oxide, or by chromic oxide. Cuprous oxide gives the intense red colour which is so well known. Uranic oxide forms a fluorescent yellow glass. Gold and stannic oxide give a red colour, and yellow is obtained by silver oxide mixed with antimonic oxide.

Neutral salts of soda are precipitated by a solution of potassic antimoniate, the sodic antimoniate being very nearly insoluble in water. The precipitate, after removal of its water of crystallization by heat, has the composition

$$Sb^2O^7Na^2H^2.$$

**221. Lithium** (Li = 7; sp. gr. 0.59; melting-point, 180°). This metal occurs as a basic constituent of many minerals, but it does not form a large per centage of any of them. Triphilline or petatile are the minerals usually employed for its preparation. The metal is obtained from its fused chloride by electrolysis.

Lithia ($Li^2O$) is a strong base, similar in its general

reactions to potash or soda. Its hydrate (H O Li) is not decomposed by heat.

Lithic carbonate is but slightly soluble in water. On the other hand, its chloride forms with platinic chloride a double salt ($Pt\,Cl^6\,Li^2$), which is even more soluble in water and in alcohol t an the corresponding salt of sodium.

Lithic phosphate ($Po^4\,Li^3$) is almost insoluble in water but readily soluble in acids. This salt frequently contains sodium in place of a part of its lithium.

Lithium is best detected by the beautiful crimson colour which its chloride imparts to flame.

Lithic chloride is soluble in a mixture of alcohol and ether, and is thus separated from chloride of sodium, which is not soluble in that mixture.

**222. Rubidium, Cœsium,** and **Thallium** are metals of the same family as the alkali metals. All these have been discovered within the last few years by the peculiar lines which their light volatile compounds give in the spectrum—rubidium giving a red line, cœsium a couple of blue lines, and thallium a green line.

Rubidium forms a platinum salt less soluble in water than the platinum salt of potassium; and cœsium forms a still less soluble platinum salt. It is by the aid of these salts that compounds of these metals are separated from salts of potassium, with which they usually occur.

Thallium has been found most abundantly in certain varieties of pyrites, and the metal itself has considerable resemblance to lead in its physical properties. Its density is 11.9, and it melts at 283°; but its specific heat and the characters of its salts leave no room for doubt that it is monatomic in its ordinary salts and triatomic in some others.

Thallium is precipitable by zinc from a solution of its sulphate. Ammonia sulphide precipitates dark brown thallic sulphide from solutions of its salts. Thallium becomes

tarnished when exposed to the air, and has a decidedly alkaline taste like potash when placed upon the tongue. Its oxide ($Tl^2O$) is soluble in water, and absorbs carbonic acid from the air.

Thallic chloride ($Tl\,Cl$) and iodide ($Tl\,I$) are but slightly soluble in water. There seems to be also a thallic trichloride. Platinic chloride unites with thallic chloride, forming the double salt $PtCl^6Tl^2$, which is considerably less soluble in water than the corresponding platinum salt of cœsium.

Thallic sulphate unites with aluminic sulphate, forming the salt $(SO^4)^4Al^2Tl^2(H^2O)^{24}$, which is a true alum. The salts of thallium are exceedingly poisonous.

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# CHAPTER XXXIV.

## ORGANIC CHEMISTRY.

**223.** Many acids, bases, and neutral compounds are usually obtained from plants or animals to whose organism they belong. Thus, citric acid is prepared from lemons, tartaric acid from grapes, formic acid from ants, albumen or gelatin from animals; sugar, starch, gum, resin and essential oils, &c. from plants; quinine, morphine, &c. also from plants. These substances were called 'organic' to denote their origin in living organisms.

Other substances are made from materials derived from animals or plants, and not from mineral materials, such as those which are employed for the formation of inorganic compounds. Thus oxalic acid is usually made from starch or from woody fibre, and formic acid from oxalic; alcohol is made from sugar, and olefiant gas is made from alcohol;

acetic acid is also made from sugar, and acetone or marsh gas are made from acetic acid; lactic acid or butyric acids are made from sugar; glycerine is made from fat, and propylene is made from glycerine. The term 'organic' has been extended to these bodies, inasmuch as they come from animals or plants, although not directly like the first-named class, but indirectly.

All of these bodies, whether themselves extracted from vital organisms, or derived from others so extracted, are found to contain carbon, and most of them contain hydrogen and oxygen also. Not a few contain nitrogen, in addition to carbon, hydrogen and oxygen. All of them are destroyed by the action of a high temperature; for they pass over into other compounds, usually termed products of destructive distillation, which do not on cooling return to the state of combination in which they occurred in the organic compounds.

Thus wood when distilled yields a mixture of various gaseous compounds, accompanied by tarry matter and acetic acid, acetone, methylic alcohol, benzole, &c., while carbon is left behind in the retort in which the wood was heated; and it is impossible to reunite these various products so as to recover the woody fibre from which they were made.

Some mineral substances are, no doubt, also decomposed by heat, forming products of decomposition which are unable to reunite on cooling so as to reproduce the compound whose decomposition gave rise to them.

Thus pyrites gives off when heated some of the sulphur contained in it, and the lower sulphide which is left does not combine with the free sulphur to reproduce pyrites. Silver oxide is decomposed by heat into metallic silver and oxygen, and these products do not recombine on cooling.

Ammonia is decomposed by a strong heat into a mixture of free nitrogen and hydrogen, which does not recombine on cooling.

On the other hand, the greater number of decompositions and other changes of mineral bodies, effected by the action of rise of temperature, are reversed by mere cooling. Thus, common phosphoric acid (trihydric phosphate) decomposes when heated, forming water and hydric phosphate; but the two bodies recombine if put together in the cold. Calcic hydrate is decomposed by heat into lime and water, but the products unite again to form the original hydrate as soon as they are brought together. Hydrosodic sulphate is decomposed by heat into sodic sulphate and hydric sulphate, but if the products be left together in the cold they reunite to form the original double salt. Hydric sulphate itself is believed to decompose on evaporation, into water and anhydrous acid, but these bodies combine again to form the original sulphate during the process of cooling. Mineral compounds are expanded by heat, and many are transformed by rise of temperature into liquids, and these in their turn, by still further heating, into vapours; but on cooling the vapour contracts and condenses to the original liquid; this, in its turn, returns on sufficient cooling to the original solid state.

The difference between organic and inorganic compounds with respect to heat may be thus summed up: That whereas all organic bodies are decomposed by heat, the great majority of mineral bodies are not permanently decomposed by it.

**224. Organic molecules** are more complicated in their structure than mineral compounds, and this characteristic distinction between the two great divisions of chemistry has been admirably embodied in Liebig's dictum—"Organic chemistry is the chemistry of compound radicals." Nothing indeed is more remarkable than the extension which the theory of radicals has undergone of late years, side by side with the extension of our knowledge of organic bodies, and organic bodies are only explained by shewing what radicals they contain. If compound radicals belonged only

to organic bodies this circumstance would afford us a very simple distinction between organic and mineral chemistry, but the distinction although quite real is not absolute.

**225.** In organic chemistry we have mainly to do with compound radicals which act like elements; whereas in mineral chemistry we meet with elementary bodies uniting in their individual capacity, as well as groups of elements which act like elementary atoms. Thus metallic oxides, sulphides, chlorides, bromides, iodides, nitrides, phosphides, find no parallel in organic chemistry, while metallic nitrates, sulphates, phosphates, &c., may be compared to the metallic acetates, tartrates, citrates. In the formula $AgNO^3$ for argentic nitrate we may consider that $NO^3$ is a radical, just as much as in argentic acetate the group $C^2H^3O^2$; for when a molecule of the nitrate is decomposed by potassic chloride the silver takes up an atom of chlorine in lieu of its atom the radical $NO^3$, and when the acetate is decomposed by potassic chloride the radical $C^2H^3O^2$ changes places with chlorine.

So also a sulphate $H^2SO^4$ undergoes double decompositions analogous to those of a succinate $H^2C^4H^4O^4$, and $SO^4$ is the diatomic radical of the sulphate just as much as $C^4H^4O^4$ is that of the succinate. $H^2SO^4$ may be compared to hydrochloric acid, or, in other words, represented in the type of hydrochloric acid, by considering it as formed from two molecules of hydrochloric acid ($H^2Cl^2$) by removing the two chlorine monads and replacing them by the dyad $SO^4$; and in like manner succinic acid may be represented on the hydrochloric acid type by calling it two molecules of hydrochloric acid, in which the dyad $C^4H^4C^4$ replaces two chlorine monads.

For many purposes it is more convenient to represent the arrangement of the elements of these molecules on the type of water $\begin{matrix}H\\H\end{matrix}O$, and they must then be considered as containing

radicals differing from these by having two atoms less of oxygen in their composition. Thus the sulphates viewed on the water-type contain the dyad $SO^2$, which replaces two atoms of hydrogen in two molecules of water; half of it being in the place of an atom of hydrogen which has left one molecule of water, the other half of it being in the place of an atom of hydrogen which has gone out from the second molecule of water.

Thus the two molecules may for convenience be written thus — $\begin{matrix} H \\ H \\ H \\ H \end{matrix}\begin{matrix} O \\ \\ O \\ \end{matrix}$, and hydric sulphate has got the dyad $SO^2$ in the place of the two middle atoms of hydrogen, thus—

$$\begin{matrix} H \\ SO^2 \\ H \end{matrix}\begin{matrix} O \\ O \\ \end{matrix}.$$

In like manner the succinates contain the dyad $C^4H^4O^2$ in the place of two atoms of hydrogen, one from one molecule of water, one from another: thus—$\begin{matrix} H \\ C^4H^4O^2 \\ H \end{matrix}\begin{matrix} O \\ O \\ \end{matrix}$.

In salts consisting of organic acids combined with metallic bases, these latter are really the inorganic part of the compound; and in like manner organic bases combine with mineral acids, such as hydrochloric, sulphuric, &c., but in these salts the really organic part is the radical which acts the part of basic metal.

Thus the radicals methyle ($CH^3$), ethyle ($C^2H^5$), propyl ($C^3H^7$), and others of this series, are really the hydrogens of organic chemistry; and their salts, such as methylic chloride ($CH^3Cl$), vinic chloride ($C^2H^5Cl$), &c., correspond to the mineral chlorides containing monatomic metals.

Other radicals, such as ethylene ($C^2H^4$), propylene ($C^3H^6$), &c., are dyads, like zinc, barium, &c., and form chlorides,

bromides, nitrates, &c., of which each molecule contains two atoms of chlorine, bromine, ($NO^3$), &c. (such as $C^2H^4Br^2$, $C^3H^6Br^2$, like $ZnBr^2$ or $BaBr^2$). Nor does the analogy stop here, for there are also triatomic and tetratomic radicals, and others of still higher atomicity in organic chemistry, corresponding to triatomic antimony, tetratomic tin, &c.

Glycerine affords an illustration of an organic compound containing a triatomic radical, replacing three atoms of hydrogen in three atoms of water. Its empyrical formula is $C^3H^8O^3$, and its reactions and decompositions prove it to contain the triad glycerile $C^3H^5$, thus $\begin{matrix}C^3H^5\\H^3\end{matrix}O^3$. Erithrite is a compound of a tetratomic radical of the composition $C^4H^6$. This radical replaces four atoms of hydrogen in four molecules of water, forming erithrite $\begin{matrix}C^4H^6\\H^4\end{matrix}O^4$. The nitrate of this basic body is formed by replacing the hydrogen, not belonging to the radical but to the water, by the radical $NO^2$. Its formula is $\begin{matrix}C^4H^6\\(NO^2)^4\end{matrix}O^4$. Just as platinic nitrate corresponds to the platinic hydrate $\begin{matrix}Pt\\H^4\end{matrix}O^4$, the hydrogen being replaced atom for atom by $NO^2$, forming $\begin{matrix}Pt\\(NO^2)^4\end{matrix}O^4$.

On the other hand, organic chemistry abounds in compounds of basic radicals with chlorous radicals, such as methylic acetate $\begin{matrix}CH^3\\C^2H^3O\end{matrix}O$, vinic succinate $\begin{matrix}C^4H^4O^2\\(C^2H^5)^2\end{matrix}O^2$, glycollic acetate $\begin{matrix}(C^2H^3O)^2\\C^2H^4\end{matrix}O^2$, glycollic succinate $\begin{matrix}C^4H^4O^2\\C^2H^4\end{matrix}O^2$, acetine $\begin{matrix}(C^2H^3O)^3\\C^3H^5\end{matrix}O^3$, &c.; and these bodies, built up entirely of compound radicals, are most characteristic of organic chemistry, and entitle that branch of the science to the definition which Liebig gave it.

*It* will be understood from these few examples that the constitution of organic compounds is more complicated than that of mineral compounds, and that organic compounds present greater varieties of property than mineral bodies. Thus alcohol is in organic chemistry the representative of water in mineral chemistry; but, instead of being the only body of its kind, alcohol is one term of a numerous series, varying in composition from $CH^4O$ to $C^{30}H^{62}O$, and presenting properties as different as their composition. Some alcohols are volatile fluids which have not been frozen by the greatest artificial cold to which they have been subjected, whereas others are solid wax-like bodies, fusible only at temperatures approaching the boiling-point of water. $C^{30}H^{62}O$ melts at 85°.

**226.** The formation of most organic compounds—such as sugar, woody fibre, quinine, albumen, &c.—is effected in the organism of growing plants under the influence of sunshine; and chemists for some time did nothing more than extract these products from vital organisms, and break them up into the simple products, carbonic acid, ammonia, and water, from the elements of which they were built up, or break them up less completely into products of simpler constitution than themselves, yet more complex than the ultimate products of combustion. Thus by the action of nitric acid on sugar ($C^6H^{10}O^5$) carbonic acid and water are obtained by a process of combustion at the expense of the oxygen of the acid—

$$C^6H^{10}O^5+(HNO^3)^{12}=(CO^2)^6+(HNO^3)^{12}+(H^2O)^5.$$

But by moderating the action of the acid, and using less of it, oxalic acid was prepared—

$$C^6H^{10}O^5+(HNO^3)^9=(C^2O^4H^2)^3+(HNO^2)^9+(H^2O)^2.$$

By using still less of the oxidizing agent, tartaric acid is obtained, together with a smaller quantity of oxalic acid—

$$C^6H^{10}O^5+(HNO^3)^6=C^4H^6O^6+C^2O^4H^2+$$
$$+H^2O+(HNO^2)^6.$$

And by moderating still further the oxidizing action, a substance called saccharic acid is obtained—

$$C^6H^{10}O^5 + (HNO)^3 = C^6H^{10}O^8 + (HNO^2)^3.$$

This saccharic acid is easily oxidized to tartaric acid, and thence to oxalic acid; and oxalic acid in its turn is easily oxidized still further to form carbonic acid—

$$C^6H^{10}O^8 + (HNO^3)^6 = (C^2O^4H^2)^3 + (HNO^2)^6 + (H^2O)^2;$$

$$(C^2O^4H^2)^3 + (HNO^3)^3 = (CO^2)^6 + (HNO^2)^3 + (H^2O)^3.$$

Saccharic, tartaric, and oxalic acids were classed among organic compounds because we had only made them by such processes as the partial decomposition of sugar; and oxalic acid was not considered the less entitled to rank among organic compounds from the fact that it was often made from the acid juice of the sorrel.

**227.** Later researches, however, shewed that oxalic acid can be built up artificially—without the presence of any plants, and from inorganic materials. Thus nitrogen gas passed over a hot mixture of carbon and sodic carbonate forms sodic cyanide (Na C N), while carbonic oxide escapes. From this sodic salt it is easy to prepare mercuric cyanide; and this when heated gives off cyanogen gas. Cyanogen dissolves readily in water, and the two compounds gradually decompose one another, forming amongst other products ammonia oxalate—

$$(CN)^2 + (H^2O)^4 = C^2O^4(NH^4)^2;$$

from which hydric oxalate is liberated by a mineral acid.

By the action of sodium on oxalic ether Löwig has obtained an acid, which he calls desoxalic acid; and desoxalic acid breaks up into one kind of tartaric acid and carbonic acid.

Alcohol is another product classed among organic bodies from the fact of its being obtained by a partial breaking up of sugar. For under the influence of growing yeast grape sugar breaks up partly into carbonic acid and alcohol—

$$C^6H^{12}O^6 = (C^2H^6O)^2 + (CO^2)^2.$$

But Berthelot has shewn that alcohol can be built up artificially from its elements. He first makes acetylene ($C^2H^2$) by discharging a galvanic battery in an atmosphere of hydrogen by carbon points. This acetylene he combines with copper, and he then brings it in contact with nascent hydrogen, thereby forming ethylene ($C^2H^4$); and ethylene he combines with oil of vitriol, forming the compound $C^2H^6SO^4$, from which alcohol is liberated by dilution with water and distillation.

Urea is another compound first obtained only from an organic source, but subsequently prepared from mineral materials. The number of organic compounds which we have learnt how to build up by inorganic processes is already very great, and additions are constantly being made to it; so that it is no longer customary to apply the term 'organic' only to those compounds which are derived directly or indirectly from plants or animals. Some compounds which were originally considered as organic are now usually studied among mineral compounds, and there seems a tendency in inorganic chemistry to continue this encroachment on the domain of organic chemistry, but the general distinction between the two parts of the science is not the less real nor the less marked.

**228.** The formation of complex molecules, such as sugar, albumen, &c., together with free oxygen, from carbonic acid, ammonia, and water, are, however, not the only results of the vital processes of plants; for there are processes of partial breaking up of complex organic molecules into less complex molecules by the agency of growing plants, analogous to the cases of partial breaking up which are effected by artificial means. Thus the fermentation of sugar is a transformation of its complex molecule, into a variety of simpler molecules, of which the best known are alcohol, carbonic acid, glycerine, succinic acid; and this process has been

shewn by the admirable investigations of Pasteur to be due to the growth of the so-called yeast or ferment, a plant which lives upon sugar and gives off this variety of simpler molecules by decomposition of the sugar. In like manner the formation of acetic acid from alcohol or from sugar in contact with air is effected by another plant, called mycoderma aceti.

Another ferment, called pericillium glaucum, transforms sugar into lactic acid, if a base be present with which the acid can combine; and the lactate thus formed is in its turn decomposed by another process of fermentation, giving rise to butyric acid, carbonic acid, hydrogen gas, &c. Under certain conditions sugar is broken up by a process of fermentation into mannite and a kind of gum. As far as researches have gone as yet into this most important class of phenomena, it would appear as if a great variety of elementary plants and infusoriæ were capable of effecting transformations of organic bodies by processes of fermentation or putrefaction, and that each little organism has a sphere of action peculiar to itself, being capable of decomposing particular organic compounds only. Thus calcic tartrate in presence of atmospheric oxygen serves as food for monads, bacteriums, &c., which evolve carbonic acid. If, however, oxygen be excluded from the mixture these infusoriæ die off, and vibrios are developed from germs in the liquid, and grow during the decomposition of the tartrate, and no doubt at its expense.

**229.** Water containing sugar, ammonia salts, and the ashes of yeast, soon becomes inhabited by various lower forms of living beings if merely exposed to the atmosphere. In like manner other mixtures capable of undergoing fermentation are found to contain infusoriæ and fungi, &c., after exposure to the air for some time.

On the other hand, Pasteur has shewn that all germs of

organic life in such a mixture are destroyed at a temperature of about 130°, and that the liquid may then be kept for any length of time without undergoing fermentation or putrefaction of any kind.

Moreover, no fermentation or putrefaction is started in such a liquid by air which has been passed through a red-hot tube, or which has been strained by passing through a tube filled by a porous plug of cotton wool or of gun cotton. In both of these cases the air is freed from all germs or seeds, &c., and it is found incapable in setting up the process of fermentation or of putrefaction in any liquid previously deprived of all germs of organic beings. On the other hand, it has been shewn by Pasteur that the dust strained off from the air by the cotton is sufficient to set up a process of decomposition of any suitable liquid, and that infusoriæ and fungi, &c., are found to be in active growth in the liquid during the whole continuance of its fermentation. By examination under the microscope the dust was moreover found to contain, besides the various earthy and woody particles, &c., little cellular masses precisely similar in appearance to the spores of fungi, &c.

In the course of these investigations it was found that the germs of animal life contained in milk (an alkaline liquid) are not destroyed by boiling at the ordinary atmospheric pressure. They were, however, completely destroyed by boiling the milk at a pressure of about 1140 millimeters (1.5 atmospheres), and the milk could then be kept for an indefinite time in a closed vessel without undergoing any decomposition.

# CHAPTER XXXV.

**230. Alcohol,** sometimes called vinic alcohol ($C^2H^6O$= 2 vols.; sp. gr. at 0° is 0.818, at 15° it is 0.7996; boiling-point, 78.4°). When mixed with a small quantity of water this compound is called spirits of wine, and the pure alcohol is sometimes distinguished by the name 'absolute alcohol.'

By distillation of a fermented liquid a mixture of water and alcohol can be obtained, containing as little as about 10 per cent. of water; but this mixture cannot be separated by further distillation, as the two liquids go over together in these proportions without any further division. In order to dry the alcohol further, the mixture may be distilled over dry potassic carbonate, but in order to dry it completely it ought finally to be mixed in a retort with its own weight of quick-lime in lumps, allowed to stand on the lime for several days (the retort being closed by a cork), and finally distilled off. The first portions collected contain the moisture of the apparatus, and should accordingly be rejected. Alcohol thus prepared sometimes contains volatile oils, which were contained in the materials from which the alcohol was made, or produced during the fermentation. To purify it from these admixtures it should be shaken up with animal charcoal before it is dried. Alcohol is liable to become acid by distillation in contact with air, by absorbing oxygen. It is also frequently accompanied by ammonia from the fermented liquid.

**231.** It mixes with water in all proportions, and the mixtures occupy a smaller volume than the alcohol and water occupied previous to mixing.

Tables have been constructed from careful experiments shewing the density of mixtures of alcohol and water in various proportions, and the usual way of ascertaining how much alcohol is contained in a particular sort of wine or beer, &c., is to distil a known quantity of the liquid, say 500 cubic centimeters, collecting carefully all that comes over while half of the liquid is distilled off. This distilled liquid (or distillate) is accurately measured, and its specific gravity is then determined at the temperature named in the table of specific gravities, by an aræometer, or better still, by a specific-gravity flask. A reference to the table then shews how much alcohol there is in one hundred parts of a mixture of the observed density, and from this the operator calculates how much must have been in his measured distillate, and thence how much in the 500 cubic centimeters of wine.

The term 'proof spirit' is still in use in this country among those who are not sufficiently aware of the value of the centesimal manner of describing the composition of mixtures in use among scientific persons. The strength of spirits of wine used to be tested by moistening some gunpowder with it, and then setting fire to the spirits. If the spirits of wine fired the gunpowder it was said to be 'over proof,' but if it contained too much water to produce that effect it was called 'under proof.' Proof spirits is now defined by law as containing 49.24 per cent. of alcohol. Every half per cent. of alcohol above this proportion is called one degree 'over proof.'

**232.** When alcohol is present in small quantity in water, it can be detected by saturating the mixture with potassic carbonate, when the alcohol makes its appearance as an oily stratum floating on the aqueous solution of the carbonate. The separation is the result of the fact that the carbonate is insoluble in alcohol but exceedingly soluble in water.

Alcohol does not dissolve any mineral salts which are

insoluble in water; and, as Miller has pointed out, it dissolves nearly all deliquescent salts, such as calcic chloride, nitrate, &c., and very few efflorescent salts, such as sodic carbonate, sulphate, &c.

Alcohol dissolves the elementary gases, oxygen, hydrogen, nitrogen; also nitrous oxide, ammonia, carbonic oxide, carbonic acid, and the gaseous hydrocarbons, to a considerably greater extent than water dissolves them.

Caustic potash or soda dissolves to a considerable extent in alcohol, and when exposed to the air the solutions become yellow or brown by absorbing oxygen, and forming a so-called resin of aldehyde. Potassium or sodium also dissolves in alcohol very rapidly, giving off hydrogen with considerable rise of temperature. The solution thus obtained contains the compound called potassic (or sodic) ethylate ($K C^2 H^5 O$), which remains behind in the solid state when the alcohol is distilled off from it.

Potassic ethylate is an intensely alkaline compound, possessing great analogy with potassic hydrate. It is present in the liquid obtained by dissolving potassic hydrate in alcohol, being formed by an interchange of the hydrogen of the hydrate with the group $C^2H^5$, called ethyle, of the alcohol—

$$K(H)O + H(C^2H^5)O = K(C^2H^5)O + HHO.$$

When alcohol is dropped upon molten potassic hydrate an evolution of hydrogen gas takes place, and potassic acetate is formed—

$$C^2H^6O + KHO = H^4 + KC^2H^3O^2.$$

Common sulphuric acid mixes with alcohol in all proportions, evolving considerable heat. When a mixture of the two liquids is heated, the alcohol breaks up chiefly into ether and water—

$$(C^2H^6O)^2 = C^4H^{10}O + H^2O,$$

if the acid be present in the proportion of two parts by weight

to one of the alcohol. When as much as four parts of sulphuric acid are present to one of alcohol, the decomposition which takes place on heating is chiefly into olefiant gas and water; $C^2H^6O = C^2H^4 + H^2O$.

Alcohol burns in the air with a pale blue flame. Its vapour requires three times its own volume of oxygen for combustion, as can be seen by the equation—

$$\underset{2\text{ vols.}}{C^2H^6O} + \underset{6\text{ vols.}}{O^6} = \underset{4\text{ vols.}}{(CO^2)^2} + \underset{6\text{ vols.}}{(H^2O)^3}.$$

When its vapour, mixed with an insufficient quantity of air for its complete combustion, is allowed to pass over a warm surface of metallic platinum, it undergoes a partial combustion, forming an acrid and pungent volatile compound.

Even in presence of water alcohol is readily oxidized to a limited extent. A red solution of potassic dichromate and sulphuric acid is very speedily changed to an emerald green colour by the addition of alcohol, and a peculiar sickly odour is perceived at the same time, owing to the formation of a body called aldehyde, consisting of $C^2H^4O$, or a molecule of alcohol from which two atoms of hydrogen have been burnt away. At the same time with aldehyde there is usually acetic acid formed ($C^2H^4O^2$), by the addition of an atom of oxygen to the elements of the aldehyde. Alcohol is entirely decomposed by passing its vapour slowly through a red-hot tube, a mixture of carbonic oxide, olefiant gas, marsh gas, hydrogen, besides several condensable hydrocarbons, being formed.

**233.** The action of monobasic hydrogen salts upon alcohol consists in forming water and a salt containing the radical $C^2H^5$ in place of the hydrogen of the original hydrogen salt. Thus hydrochloric acid forms water and ethylic chloride—

$$HC^2H^5O + HCl = HHO + C^2H^5Cl.$$

Hydriodic acid, in like manner, forms water and ethylic iodide—

$$H C^2H^5O + H I = H H O + C^2H^5 I.$$

Nitric acid forms water and ethylic nitrate—

$$H C^2H^5O + H N O^3 = H H O + C^2H^5 N O^3.$$

**234.** These reactions are precisely similar to those which take place between potassic hydrate and the same hydrogen salts, the group $C^2H^5$ from alcohol forming a salt as potassium does in its corresponding reactions. Thus writing K for $C^2H^5$ in the above equation we have the double decomposition between potassic hydrate and hydric nitrate, forming water and potassic nitrate—

$$H K O + H N O^3 = H H O + K N O^3.$$

Throughout all the reactions among its compounds the group $C^2H^5$ exhibits this analogy with a monatomic metal, and it is accordingly considered as a monatomic organic radical, that is, as an organic radical of which the atom as represented by the formula $C^2H^5$ is capable of replacing one atom of hydrogen in its various salts.

According to this view, the constitution of alcohol is explained by comparing it to water. If a molecule of water, H H O, were to lose one of its atoms of hydrogen and to take up an atom of ethyle in the place of that hydrogen, it would be transformed into alcohol. We shall see that alcohol is easily made by this process. It is important, moreover, to observe that inasmuch as the molecule of alcohol and the molecule of water each occupies two volumes in the state of vapour, the atom of ethyle takes exactly the space vacated by the atom of hydrogen which it replaces—

$$H H O = 2 \text{ vols.} \quad H (C^2H^5) O = 2 \text{ vols.}$$

When alcohol or any other substance is thus represented on the water-type it often becomes necessary to distinguish between the hydrogen of the ethyle and the hydrogen of the original type (water). The term 'typical hydrogen' is

used to denote hydrogen remaining from the water in any compound belonging to the water-type; or more generally a 'typical' element means an element left unreplaced in the typical body from which a compound is formed.

Bibasic acids, such as oxalic, sulphuric, &c., form not only salts containing two atoms of ethyle in one molecule of the salt, but they also form double salts containing one atom of ethyle and one atom of hydrogen in each molecule of the salt. Thus we have ethylic oxalate ($(C^2H^5)^2C^2O^4$), and hydrethylic oxalate ($H(C^2H^5)C^2O^4$). So also ethylic sulphate ($(C^2H^5)^2SO^4$), and also hydrethylic sulphate ($H(C^2H^5)SO^4$), commonly called sulphovinic acid. In like manner there is an ethylic carbonate ($(C^2H^5)^2CO^3$), and a hydrethylic carbonate ($H(C^2H^5)CO^3$) called carbovinic acid.

There are also double phosphates containing ethyle and hydrogen, in proportions corresponding to the sodium and hydrogen in the double phosphates containing those elements. Hydrodiethylic phosphate is $H(C^2H^5)^2Po^4$, dihydroethylic phosphate is $H^2C^2H^5Po^4$, and the ethylic phosphate, commonly called phosphoric ether, is $(C^2H^5)^3Po^4$.

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# CHAPTER XXXVI.

**235. Methylic Alcohol,** or wood-spirits ($CH^4O$ = 2 vols.; density at 0°, .82; boiling-point, 66°). This substance is formed, together with a variety of other liquid compounds and several gases, by the destructive distillation of wood. A considerable quantity of tar is deposited from the products which pass off from the retort in which the wood is distilled, and with this tar is water containing acetic acid and wood-spirits. This watery liquid

is usually neutralized by lime, and distilled. The crude wood-spirits come over in the beginning of the distillation accompanied by a little water, and it is usually introduced into commerce, after partial drying, by distilling over quick-lime. In this state it is usually a yellowish liquid, of an unpleasant smell. It is often called 'naphtha,' or 'wood-naphtha.' Its chief use is for mixing with spirits of wine to form the so-called methylated spirit, which manufacturers are allowed to use without paying the excise duty which is levied on other spirits of wine.

Methylated spirit contains ten per cent. of wood-spirits, and possesses the characteristic smell of that mixture.

**236.** Common **Wood-spirit** generally becomes turbid when mixed with water, owing to the precipitation of liquid hydrocarbons which were dissolved in it.

For the preparation of methylic alcohol it should be mixed with nearly its own volume of strong caustic soda-solution, and allowed to stand in a closed vessel for several hours. The liquid which in most cases collects on the surface should be removed from the alkaline mixture, and the latter distilled as long as any combustible distillate comes over. The sodic solution which is left behind contains a large quantity of sodic acetate, which was formed simultaneously with methylic alcohol by the action of the soda on methylic acetate contained in the crude wood-spirit. This distillate usually contains ammonia, and should be distilled with 3 or 4 per cent. of sulphuric acid, which not only keeps back the volatile bases but also a good deal of tarry matter formed from impurities in the wood-spirits. In this manner a mixture of methylic alcohol with water, acetone, and dimethylacetal is obtained; and to get rid of the two last-named bodies, the mixture should be saturated with dry calcic chloride, and distilled in a water-bath as long as anything comes over at that temperature. The distillate consists of

acetone dimethylacetal, and sometimes a part of the methylic alcohol; and the calcic chloride in the retort retains methylic alcohol in the form of a compound which is not decomposed when heated to 100°. In order to liberate the alcohol from this compound, water should be added in small quantity and the mixture should then be distilled. The alcohol which comes over requires subsequent drying by means similar to those described for drying common vinic alcohol.

When required in the purest obtainable state methylic alcohol is made by the action of ammonia on methylic oxalate—

$$(C H^3)^2 C^2 O^4 + (N H^3)^2 = (C H^4 O)^2 + N^2 H^4 C^2 O^2;$$

oxamide being formed at the same time.

The filtered liquid is neutralized by sulphuric acid, to take up the excess of ammonia, and distilled. The distillate consists of a mixture of water and pure **Methylic Alcohol.**

**237.** This remarkable liquid has great resemblance to vinic alcohol in its properties. It mixes with water in all proportions, and with condensation.

Potassium or sodium dissolves in it with evolution of hydrogen, forming solutions of the compounds $K C H^3 O$ or $Na C H^3 O$, called respectively potassic methylate and sodic methylate. Methylic alcohol dissolves caustic potash or soda, forming these same compounds together with water—

$$H C H^3 O + K H O = K C H^3 O + H H O.$$

Monobasic acids (hydrogen salts), such as hydrochloric, hydriodic, nitric, &c., react upon methylic alcohol in like manner as upon vinic alcohol, forming water and compounds of methyle, such as the chloride ($C H^3 Cl$), iodide ($C H^3 I$), or nitrate ($C H^3 N O^3$). In these reactions the radical methyle changes places with an atom of hydrogen, just as an atom of ethyle does in the corresponding reactions of these acids on vinic alcohol, and a molecule of water is formed in each case from a molecule of methylic alcohol, by the replacement of

its methyle by hydrogen, the vapour-volume being unaltered by the interchange—

$$\overset{2\text{ vols.}}{H(CH^3)O} + \overset{2\text{ vols.}}{HCl} = \overset{2\text{ vols.}}{HHO} + \overset{2\text{ vols.}}{(CH^3)Cl}.$$

Bibasic acids form both normal salts with methyle, such as

$(CH^3)^2C^2O^4$, methylic oxalate;
$(CH^3)^2SO^4$, methylic sulphate;
$(CH^3)^2CO^3$, methylic carbonate:

and also double salts, such as

$HCH^3C^2O^4$, hydromethylic oxalate or oxalomethylic acid;
$HCH^3SO^4$, hydromethylic sulphate or sulphomethylic acid;
$HCH^3CO^3$, hydromethylic carbonate or carbomethylic acid.

Tribasic acids, such as phosphoric acid, form not only normal methyle salts, containing three atoms of methyle ($(CH^3)^3$) in each molecule of the salt, such as methylic phosphate $(CH^3)^3PO^4$; they also form two classes of double salts: one, in which one-third of the methyle is replaced by hydrogen or a metal, such as the hydrodimethylic phosphate $H(CH^3)^2PO^4$; another, in which two-thirds of the methyle are so replaced, as in the case of the dihydromethylic phosphate $H^2CH^3PO^4$.

Sulphuric acid when heated with one-quarter its weight of methylic alcohol decomposes it into so-called methylic ether ($C^2H^6O$) and water—

$$(HCH^3O)^2 = C^2H^6O + HHO.$$

Carbonic acid, sulphurous acid, and other products are formed at the same time. All attempts to form from methylic alcohol the hydrocarbon $CH^2$, as olefiant gas is formed from vinic alcohol, have failed.

**238.** Methylic alcohol is admitted to be constituted like vinic alcohol, having the radical methyle ($CH^3$) in the place of the ethyle ($C^2H^5$) of vinic alcohol; and similar arguments to those which served to establish that vinic alcohol is a molecule of water (HHO) in which one atom of hydrogen

is replaced by an atom of ethyle ($(C^2H^5)HO$) may be used to prove that methylic alcohol is formed from water by the replacement of one atom of hydrogen by methyle ($(CH^3)HO$).

The two alcohols differ empirically in composition by the elements $CH^2$; for if these were taken from vinic alcohol without disarranging the remaining elements, methylic alcohol would be formed ($C^2H^6O - CH^2 = CH^4O$).

The term '**homologous**' is used to denote bodies possessing analogous properties, as shewn by their reactions, and differing from one another by $CH^2$, or any multiple of $CH^2$. It was stated above that the action of sulphuric acid upon methylic alcohol gives rise to the formation of a product having a composition represented by the empirical formula $C^2H^6O$. The density of this compound in the state of vapour is identical with that of alcohol vapour—

$$C^2H^6O = 2 \text{ vols.};$$

but this methylic ether is a vapour at the common atmospheric temperature, and when condensed to the liquid state is found to have the boiling-point $-23.5°C$, whilst vinic alcohol boils at $78°$.

The study of the reactions of methylic ether shews that its constitution is not perfectly analogous to that of methylic alcohol, so that it is not homologous with it. For each molecule of methylic ether is found to contain two atoms of methyle ($(CH^3)^2O$), of which one or both can be removed and replaced by hydrogen, atom for atom; and in no reactions does it shew a behaviour like alcohol, which retains from the water an atom of hydrogen replaceable by potassium.

**239.** Under the action of oxidizing agents, or of molten potassic hydrate, methylic alcohol gives rise to the formation of formiates, such as the hydric formiate $HCHO^2$. These formiates are analogous in their constitution to the acetates (such as hydric acetate, $HC^2H^3O^2$), and accordingly the two acids afford us a second instance of homology.

By limiting the action of oxidising agents on methylic alcohol no product of the composition $CH^2O$, corresponding to aldehyde, has ever been obtained.

Four other alcohols have been found in the fermented 'mark' of the grape. This substance consists of the skins, seeds, and stalks of grapes from which the juice has been expressed for the manufacture of wine. When allowed to ferment the mass yields vinic alcohol, which is sold as brandy; but with this brandy there is a substance known by the name of fousel oil, which comes over mostly at the end of the distillation. This fousel oil has been found to contain propylic alcohol ($HC^3H^7O$), sometimes called tritylic, and amylic alcohol ($HC^5H^{11}O$), and caproic alcohol ($HC^6H^{13}O$), sometimes called hexylic. Different specimens of the fousel oil contain these bodies in different proportions, and they are separated from one another by oft-repeated fractional distillations. Butylic alcohol ($C^4H^{10}O$) has been found in some specimens of fousel oil made from potato spirits, as well as from the fousel oil of beetroot molasses. The most advantageous form of apparatus for this purpose is found to be a flask with a very long neck, near the top of which is the bulb of a thermometer. The top of the neck communicates with a condenser, in which the most volatile constituents of the distilling mixture are collected; whilst the less volatile constituents are condensed in the neck of the flask, and run back into the boiling liquid.

**240.** Propylic alcohol ($C^3H^8O$ = 2 vols.; boiling-point, 96°). This body is not miscible with water in all proportions, although water dissolves a great deal of it. Its reactions are in all respects analogous to those of vinic alcohol, and it is considered to contain the radical propyl ($C^3H^7$) in the same manner that vinic alcohol contains the radical ethyle. It is therefore homologous with methylic and vinic alcohols, and is the third term of the series of alcohols. Its deriva-

*tives*—propylic chloride ($C^3H^7Cl$), propylic iodide ($C^3H^7I$), propylic nitrate ($C^3H^7NO^3$), hydropropylic sulphate ($HC^3H^7SO^4$), &c.—are homologous with the corresponding methyle and ethyle compounds.

A substance of the same composition as propylic alcohol has been formed by the action of sodium amalgam upon acetone in presence of water. Acetone contains only six atoms of hydrogen in each molecule, its formula being $C^3H^6O$, so that the propylic alcohol is formed by the addition of two atoms of hydrogen to acetone. The alcohol thus obtained differs in some respects from that found in the mark. Its boiling-point is below 90°. The same product seems to be formed from acrolein by a similar treatment. Acrolein is composed of $C^3H^4O$, and sodium amalgam in presence of water adds to it hydrogen, forming two liquids of like composition ($C^3H^8O$), but differing from one another by their boiling-points—one of them boiling between 87° and 88°, while the other boils between 96° and 98°. The former of these is supposed to be identical with the product formed from acetone, and the latter identical with propylic alcohol.

The hydrocarbon propylene ($C^3H^6$) is absorbed rapidly by oil of vitriol, and the solution when distilled with water yields a distillate containing an alcohol of the composition $C^3H^8O$, and boiling at 85°.

It has been found that this propylic alcohol breaks up more easily into propylene and water than is the case with the propylic alcohol formed by fermentation, and it is considered probable that the alcohol made from acetone may be identical with this one made from propylene.

Propylic alcohol can be oxidised like vinic alcohol, yielding propylic aldehyde ($C^3H^6O$), a body isomeric but not identical with acetone; and by further oxidation it yields so-called propionic acid.

# CHAPTER XXXVII.

**241. Butylic Alcohol** ($H C^4 H^9 O = 2$ vols.; boiling-point, 106° to 109°) has been prepared from the fousel oil obtained in the distillation of spirits from fermented beetroot.

Its reactions are analogous to those of vinic alcohol, and it is considered to be a molecule of water in which one atom of hydrogen is replaced by the radical butyl $C^4 H^9$.

A volatile compound of the composition $C^4 H^9 I = 2$ vols., boiling at 117 to 118°, has been obtained by the action of hydriodic acid on erithrite ($C^4 H^{10} O^4$). It has been shewn that this compound is isomeric with butylic iodide prepared from butylic alcohol. The alcohol prepared from it boils at 96 to 98°.

By the action of oxidizing agents, such as fused potash, &c., butylic alcohol yields compounds of an acid homologous with acetic acid, and containing in each of its salts $C^2 H^4$ more than in the corresponding acetate. The hydrogen salt of this acid has been found in rancid butter, and obtained thence the name butyric acid; its formula is $H C^4 H^7 O^2$.

**242. Amylic Alcohol** ($H C^5 H^{11} O = 2$ vols.; boiling-point, 129 to 132°). This alcohol is the commonest constituent of fousel oil, and is easily obtained in quantity from that source. It has an exceedingly unpleasant odour, which is said to produce headache if much inhaled. Water dissolves it but slightly, and it floats upon water like an oil. Potassium displaces one atom of hydrogen in amylic alcohol, forming a solution of potassic amylate ($K C^5 H^{11} O$) in the alcohol. The common hydrogen salts decompose amylic alcohol, forming water and compounds of the radical amyle, such as amylic chloride ($C^5 H^{11} Cl$), hydramylic sulphate ($H C^5 H^{11} S O^4$), &c.; and

there is no doubt that it is analogous in its constitution to the true alcohols, and contains the radical amyle $C^5H^{11}$ in the place of one atom of hydrogen of water.

When heated with sulphuric acid amylic alcohol does not, however, yield an ether as vinic alcohol does. The mixture becomes black—gives off sulphurous and carbonic acids, together with products of the destruction of the amylic compound.

Still less does amylic alcohol yield a gas homologous with olefiant gas when treated with a greater quantity of strong sulphuric acid. When, however, amylic alcohol is mixed with zinc chloride in the proportion of $1\frac{1}{2}$ times its weight, and after standing two or three days, carefully distilled, a mixture of volatile products is obtained, containing amylene—

($C^5H^{10}$ = 2 vols.),

which boils at 35°, and has a specific gravity of .663 at 0°. This body is proved by its reactions to be the olefiant gas of amylic alcohol, and is less volatile than olefiant gas itself in consequence of its greater molecular weight.

A mixture of oil of vitriol with one-quarter of its volume of water dissolves amylene, forming sulphamylic acid, and by diluting this liquid with water and distilling, an alcohol is set free, differing from amylic alcohol formed by fermentation by its greater tendency to break up into amylene and water.

The ether of amylic alcohol (amylic oxide, $C^{10}H^{22}O$) has been obtained by another process, and found to boil at 176°, a circumstance which sufficiently accounts for its not being obtainable by heat from a mixture of the alcohol with sulphuric acid, as the ether is burnt by sulphuric acid at a lower temperature than its boiling-point. Pasteur has found that in fousel oil there are two isomeric amylic alcohols; one of them rotating the ray of polarized light, boiling at 127° to 128°, while the other has no rotating action on the ray, and boils at 129°. By combining these two alcohols with

sulphuric acid and neutralizing the compound (hydramylic sulphate, $HC^5H^{11}SO^4$) by baryta, salts were obtained of like composition ($Ba(C^5H^{11}SO^4)^2$), but differing from one another in their solubility in water; the salt made from the rotating alcohol being $2\frac{1}{2}$ times as soluble as that made from the inactive alcohol.

By the action of an aqueous solution of chromic acid mixed with sulphuric acid fousel oil is oxidized, forming a mixture of valerianic acid ($C^5H^{10}O^2$) and valerianic aldehyde ($C^5H^{10}O$); the former an acid homologous with acetic acid and boiling at 176°, the latter a neutral body which combines with hydrosodic sulphite. The aldehyde boils at 96°; in contact with oxygen it is readily transformed into valerianic acid.

**243. Caproic Alcohol** ($HC^6H^{13}O$ = 2 vols.; boiling-point, 154° to 166°) has been obtained in small quantities from the mark of the grape. By distilling mannite ($C^6H^{14}O^6$) with an aqueous solution of hydriodic acid, Wanklyn has obtained a volatile oil of the composition $C^6H^{13}I$ = 2 vols., from which so-called hexylic alcohol ($HC^6H^{13}O$) has been obtained isomeric with the alcohol obtained from the mark. An acid of the composition $C^6H^{12}O^2$, called caproic acid, has been found in butter and several other fatty mixtures. It stands to caproic alcohol in the same relation in which acetic acid stands to vinic alcohol—

$$C^6H^{14}O - H^2 + O = C^6H^{12}O^2.$$

Œnanthic alcohol ($C^7H^{16}O$) appears to be formed in some cases by distilling castor-oil soap with potassic hydrate.

Its aldehyde, called œnanthol ($C^7H^{14}O$), is found among the products of the dry distillation of castor oil, and is separated from the oily products accompanying it by distilling the mixture with steam, which carries over the œnanthol accompanied by a little impurity, and a repetition of the distillation with water renders it still purer.

By the action of nitric acid on castor oil a volatile acid is formed, which distils over with water from the retort in which the oxidation takes place. This oily acid has the composition $C^7H^{14}O^2$, and is called œnanthylic acid.

Caprilic alcohol ($C^8H^{18}O$ = 2 vols.; boiling-point, 178°) was discovered by M. Bouis in the distillation of castor-oil soap with potassic hydrate. Potassic sebate remains behind in the retort—

Potassic ricinoleate Potassic sebate

$$\overbrace{C^{18}H^{33}KO^3}+KH^3O^2 = C^8H^{18}O+\overbrace{C^{10}H^{16}K^2O^4}+H^2.$$

Caprilic acid ($C^8H^{16}O^2$) has been found in butter and in cocoa-nut oil.

**244. Cetylic Alcohol** ($C^{16}H^{34}O$) is derived from a beautiful crystalline compound known by the name of spermaceti, which is found with other fats in the heads of whales. Potassic hydrate melted with a little water decomposes this compound, easily forming potassic palmitate ($C^{16}H^{31}KO^2$) and cetylic alcohol. The decomposition is effected at a lower temperature by the aid of alcohol. The alcohol can be obtained by precipitating the palmitate by calcic chloride, forming calcic palmitate, which carries down the cetylic alcohol with it. Ether dissolves the alcohol, leaving the palmitate. Cetylic alcohol melts at 49°.

By distilling cetylic alcohol with anhydrous phosphoric acid a hydrocarbon of the compositon $C^{16}H^{32}$ is obtained. This olefiant gas of cetylic alcohol boils at about 275°.

Spermaceti has the empirical composition $C^{32}H^{64}O^2$, and its rational formula is $\begin{matrix}C^{16}H^{33}\\C^{16}H^{31}\end{matrix}O$, which represents it as cetylic palmitate. Potassic hydrate puts an atom of potassium into this group in lieu of an atom of the radical cetyle—

$$\begin{matrix}C^{16}H^{31}\\C^{16}H^{33}\end{matrix}O+\begin{matrix}H\\K\end{matrix}O = \begin{matrix}C^{16}H^{31}\\K\end{matrix}O+\begin{matrix}H\\C^{16}H^{33}\end{matrix}O.$$

Palmitic acid is the chief solid constituent of so-called palm oil, which is now so largely imported for the manufacture of soap, &c.

**245. Cerotic Alcohol** ($C^{27}H^{56}O$) has been prepared by Brodie from Chinese wax, by a decomposition similar to that by which cetylic alcohol was obtained from spermaceti.

Potassic cerotate ($C^{27}H^{53}KO^2$) is obtained at the same time. Cerotic alcohol is a hard and brittle solid, insoluble in water, but soluble in alcohol and ether. It melts at 97°.

A solid hydrocarbon has been obtained from Chinese wax, possessing probably the composition $C^{27}H^{54}$. It melts between 57° and 58°. In its properties this substance has great resemblance to the mixtures now so much used by the name of **Paraffine,** which are found among the products of dry distillation of boghead, or cannel coal, and various bituminous schists.

Cerotic acid ($C^{27}H^{54}O^2$) is found in several varieties of beeswax, and is extracted from that substance by boiling alcohol. It melts at 78°.

**Melissic Alcohol** ($C^{30}H^{62}O$) is the highest term now known of the alcohol series. It was prepared by Brodie from melissic palmitate— $\begin{matrix}C^{30}H^{61}\\C^{16}H^{31}O\end{matrix}O$, a constituent of beeswax, by the action of potassic hydrate.

It is partly decomposed by distillation, water being formed, together with a beautiful hydrocarbon ($C^{30}H^{60}$), which melts at 62°.

Molten potassic hydrate oxidizes melissic alcohol, forming a potash salt of melissic acid with evolution of hydrogen—

$$\begin{matrix}C^{30}H^{61}\\H\end{matrix}O+\begin{matrix}H\\K\end{matrix}O=\begin{matrix}C^{30}H^{59}O\\K\end{matrix}O+H^4.$$

# CHAPTER XXXVIII.

**246. Ether** ($C^4H^{10}O$ = 2 vols.; boiling-point, 35°) is formed by the replacement of two atoms of hydrogen in a molecule of water by two atoms of ethyle. From alcohol it is made by displacing the typical hydrogen by sodium, and acting on the sodic ethylate thus obtained by vinic iodide. The first reaction is this— $\begin{matrix}C^2H^5\\H\end{matrix}O + Na = \begin{matrix}C^2H^5\\Na\end{matrix}O + H.$ The second is this— $\begin{matrix}C^2H^5\\Na\end{matrix}O + C^2H^5I = \begin{matrix}C^2H^5\\C^2H^5\end{matrix}O + KI.$

It is commonly prepared by the action of strong sulphuric acid on alcohol. When two volumes of strong spirits of wine are mixed with three volumes of sulphuric acid, considerable heat is evolved, and the mixture contains sulphovinic acid and water as well as sulphuric acid and alcohol. These products are formed by the exchange of one atom of hydrogen in sulphuric acid for an atom of ethyle in the alcohol—

$$\begin{matrix}H\\H\end{matrix}SO^4 + \begin{matrix}H\\C^2H^5\end{matrix}O = \begin{matrix}H\\C^2H^5\end{matrix}SO^4 + \begin{matrix}H\\H\end{matrix}O.$$

When the mixture of these four compounds is heated to about 135°C a second reaction takes place, forming ether and reproducing sulphuric acid. This second reaction consists of an interchange between ethyle in the sulphovinic acid and typical hydrogen in alcohol: thus—

$$\begin{matrix}H\\C^2H^5\end{matrix}SO^4 + \begin{matrix}C^2H^5\\H\end{matrix}O = \begin{matrix}C^2H^5\\C^2H^5\end{matrix}O + \begin{matrix}H\\H\end{matrix}SO^4.$$

The ether thus formed evaporates, and must be collected by a suitable condenser. The sulphuric acid which is reproduced at the end of the process is usually employed for

the transformation of more alcohol into ether and water, and for that purpose it is kept at the same temperature of 135°, while alcohol is allowed to flow into it slowly by a tube reaching to the bottom of the vessel containing the acid. The flow of alcohol should be regulated so as to keep the surface of the mixture in the retort constantly at its initial height.

**247.** The alcohol which comes in contact with this sulphuric acid reacts in the same manner as that which was first mixed with it—forming water, which distils off, and sulphovinic acid; and this sulphovinic acid in its turn reacts on another molecule of alcohol, forming ether and sulphuric acid. Thus it is that a given quantity of acid transforms an indefinite quantity of alcohol into these two products. The acid is renewed occasionally, because it gets contaminated by impurities in the alcohol, and by secondary products, which impair its action.

The liquid collected in the receiver consists of two strata; the lower one being chiefly water, the upper stratum impure ether. Sulphurous acid is usually present in the distillate, and is removed by washing the ether by caustic soda; alcohol is always carried over with the ether and water, and can be partially removed by washing with salt water, in which it is far more soluble than ether. To obtain the ether pure it should be finally distilled over powdered sodic hydrate, or even metallic sodium, which keep back any water or alcohol.

**248.** Ether is an exceedingly mobile liquid, of 0.736 density at 0°. It has an agreeable odour, which is well known under the name 'ethereal.' It produces an anæsthetic effect when inhaled in sufficient quantity, but its use for this purpose has been given up, owing to the unpleasant after-effects which it produces on the patient. It dissolves in about fourteen times its volume of water; but if there be not

water enough to dissolve it, the supernatent stratum of ether takes up about $\frac{1}{36}$ of its volume of water, which it holds in solution. When poured on the hand ether produces a strong sensation of cold, owing to the rapidity with which it evaporates, rendering heat latent. Its vapour density is 37, as can be seen from the fact that its molecule ($C^4H^{10}O$), weighing 74, occupies 2 volumes in the state of vapour.

Being about $2\frac{1}{2}$ times as heavy as air, ether vapour can easily be poured from one vessel to another.

It very easily catches fire, and burns with a white flame. A mixture of ether vapour and air explodes with great violence if containing oxygen in about the combining proportions, viz. six volumes to every one of ether vapour. Ether ought never to be distilled in the vicinity of fire or flame, but hot water should be brought from a distance to pour into a vessel in which the retort full of ether is contained.

Ether dissolves oils, and fats, and resins far more readily than alcohol dissolves them.

Sulphur, phosphorus, and iodine dissolve in ether.

Metallic salts are as a rule less soluble in ether than in alcohol, and many salts which dissolve readily in alcohol can be precipitated from that solution by the addition of ether. Strong sulphuric acid dissolves ether readily, doubtless forming alcohol and sulphovinic acid—

$$\begin{matrix} C^2H^5 \\ C^2H^5 \end{matrix}O + \begin{matrix} H \\ H \end{matrix}SO^4 = \begin{matrix} H^2 \\ C^2H^5 \end{matrix}O + \begin{matrix} C^2H^5 \\ H \end{matrix}SO^4;$$

and probably also water and a second molecule of sulphovinic acid.

Anhydrous sulphuric acid combines with ether as with water, forming vinic sulphate $\begin{matrix} C^2H^5 \\ C^2H^5 \end{matrix}SO^4$.

**249. Methylic Ether** ($C^2H^6O$ = 2 vols.; boiling-point, −23.6°). This gas is obtained from methylic alcohol by

processes similar to those described for the preparation of vinic ether from its alcohol. Water dissolves between 30 and 40 times its volume of methylic ether at the ordinary temperature.

**Vinomethylic Ether** $\left(\begin{matrix}C^2H^5\\C\ H^3\end{matrix}O = 2\right.$ vols.; boiling-point, $\left.11°\right)$ is formed by the action of methylic iodide on potassic ethylate—

$$C\,H^3I + \begin{matrix}C^2H^5\\K\end{matrix}O = KI + \begin{matrix}C^2H^5\\C\,H^3\end{matrix}O;$$

or by the equivalent reaction of vinic iodide on potassic methylate—

$$C^2H^3I + \begin{matrix}K\\C\,H^3\end{matrix}O = KI + \begin{matrix}C^2H^5\\C\ H^3\end{matrix}O.$$

It is also formed by the action of methylic alcohol on a mixture of strong sulphuric acid with vinic alcohol. The sulphuric acid contained in this mixture replaces the typical hydrogen of the methylic alcohol by ethyle, just as it replaces the typical hydrogen of vinic alcohol by ethyle in the formation of vinic ether—

$$\begin{matrix}H\\C\,H^3\end{matrix}O + \begin{matrix}C^2H^5\\H\end{matrix}SO^4 = \begin{matrix}C^2H^5\\C\ H^3\end{matrix}O + \begin{matrix}H\\H\end{matrix}SO^4.$$

This ether has an agreeable odour, easily distinguishable from that of common ether.

Propylic ether $\left(\begin{matrix}C^3H^7\\C^3H^7\end{matrix}O\right)$ and butylic ether $\left(\begin{matrix}C^4H^9\\C^4H^9\end{matrix}O\right)$, are but little known.

Amylic ether ($C^{10}H^{22}O$ = 2 vols.; boiling-point, 176°) cannot be obtained by distilling sulphuric acid with amylic alcohol, but it has been prepared by the action of amylic iodide on potassic amylate—

$$C^5H^{11}I + \begin{matrix}K\\C^5H^{11}\end{matrix}O = KI + \begin{matrix}C^5H^{11}\\C^5H^{11}\end{matrix}O.$$

And this mode of formation leaves no doubt as to the fact that its constitution is analogous to that of the lower ethers.

**250.** Amylomethylic ether $\left(\begin{matrix}C^5H^{11}\\C\ H^3\end{matrix}O\right.$; boiling-point, 92°$\left.\right)$ is obtained by the action of methylic iodide on potassic amylate, or by distilling a mixture of equivalent weights of amylic and methylic alcohols with strong sulphuric acid, allowing the mixed alcohols to flow gradually into the boiling mixture, as vinic alcohol is allowed to flow in during the common continuous process of etherification.

Amylovinic ether $\left(\begin{matrix}C^5H^{11}\\C^2H^5\end{matrix}O\right.$ = 2 vols.; boiling-point, 112°$\left.\right)$ has been obtained by perfectly similar processes, from the vinic and amylic alcohols.

**251.** The higher ethers of the alcohol series are but little known. The formation and constitution of ethers have taught us the important fact that the oxide of a monatomic element or radical contains in each molecule two monads, and that the compound of water with the oxide of a monad does not contain in each molecule the elements of one molecule of the oxide plus the elements of one molecule of water, but only half of that quantity.

Thus alcohol, which is truly the compound of water with ethylic oxide, $(C^2H^5)^2O$, does not contain a complete molecule of ether plus a complete molecule of water in each of its own molecules, for two molecules of alcohol must concur to form one of ether plus one of water. It is not long since chemists believed that ether and water were formed by the mere cutting in two of a molecule of alcohol; and while so representing the process, they consistently assumed that the oxygen in each molecule (weighing 16) was not one atom, but two atoms, each weighing 8. Thus using the symbol $\frac{O}{2} = 8$, we should represent ether as $C^2H^5\frac{O}{2}$, water as $H\frac{O}{2}$, and alcohol as $\begin{matrix}C^2H^5\frac{O}{2}\\H\frac{O}{2}\end{matrix}$; methylic alcohol would be $\begin{matrix}C\ H^3\frac{O}{2}\\H\frac{O}{2}\end{matrix}$, and methylic oxide $C\,H^3\frac{O}{2}$: and according to

this system each molecule of water, methylic oxide, or vinic oxide would occupy one volume, while each molecule of the alcohols would occupy two volumes, like a molecule of vinic or methylic iodide. The formation of common ether by the action of vinic iodide on potassic ethylate would be represented as an interchange between potassium in the one and ethyle in the other molecule; such exchange being accompanied by a breaking up of the molecule $\begin{matrix} C^2H^5\frac{O}{2} \\ C^2H^5\frac{O}{2} \end{matrix}$ into two molecules of the composition $C^2H^5\frac{O}{2}$.

But this explanation would assume the occurrence of a process of breaking up, which is proved not to occur in the closely analogous case of the formation of methylovinic ether, by the action of methylic iodide on potassic ethylate. In this case the compound $\begin{matrix} C^2H^5\frac{O}{2} \\ C\ H^3\frac{O}{2} \end{matrix}$ does not break up into $C^2H^5\frac{O}{2}$ and $C\,H^3\frac{O}{2}$.

In like manner, when sulphuric acid reacts upon alcohol, forming sulphuric acid and ether, the process would have to be represented as an interchange of ethyle in the acid with hydrogen in the alcohol, and as a breaking up of the ether into two molecules. It is found in every case in which the radical contained in the acid can be distinguished from the radical contained in the alcohol, that the two go into the composition of one molecule of ether.

When sulphovinic acid is boiled with water an interchange of ethyle in the acid and hydrogen in the water takes place, forming sulphuric acid and alcohol; and if the molecule of water were $H\frac{O}{2}$, the process could not be explained without assuming that the ether $C^2H^5\frac{O}{2}$ combines at the moment of its formation with a molecule of water to form a molecule of alcohol.

Not only would the analogous bodies—water, alcohols, ethers, &c.—be represented in this manner by dissimilar

formulæ, some containing $\frac{O}{2}$ in one molecule, others two small atoms of oxygen in each molecule—

$H\frac{O}{2}$, $CH^{3}O$, $C^{2}H^{5}\frac{O}{2}$, $C^{2}H^{5}H\frac{O}{2}\frac{O}{2}$, $CH^{3}H\frac{O}{2}\frac{O}{2}$, &c.;

$CH^{3}C^{2}H^{5}\frac{O}{2}\frac{O}{2}$, $C^{2}H^{5}C^{6}H^{11}\frac{O}{2}\frac{O}{2}$, &c.;

but it would be necessary to assume, besides the interchanges which are known to take place, a number of separations and combinations among the products of these interchanges, combinations and separations which are proved to have no existence in closely analogous cases.

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# CHAPTER XXXIX.

**252.** The analogy between oxygen and sulphur, between sulphur and selenium, and between selenium and tellurium, naturally suggests the probability of these elements being able to replace oxygen, atom for atom, in the alcohols and ethers—forming sulphides, selenides, tellurides, &c. analogous to these oxides. As far as experiments have gone as yet these anticipations have been confirmed.

**Hydromethylic Sulphide,** or methylic mercaptan $\left(\begin{matrix}CH^{3}\\H\end{matrix}S = 2 \text{ vols.}\right.$; boiling-point, 21°$\left.\right)$, is formed by distilling a mixture of methylocalcic sulphate and hydropotassic sulphide—

$$\begin{matrix}Ca\\(CH^{3})^{2}\end{matrix}(SO^{4})^{2} + \begin{matrix}H^{2}\\K^{2}\end{matrix}S^{2} = \left(\begin{matrix}CH^{3}\\H\end{matrix}S\right)^{2} + K^{2}SO^{4} + CaSO^{4}.$$

It is more easily formed by the action of methylic iodide upon an alcoholic solution of potassic sulphydrate—

$$CH^{3}I + \begin{matrix}H\\K\end{matrix}S = \begin{matrix}CH^{3}\\H\end{matrix}S + KI.$$

When potassic sulphide is used instead of hydropotassic sulphide, the product is methylic sulphide ($(CH^3)^2S$ = 2 vols.)—

$$K^2S + (CH^3I)^2 = (CH^3)^2S + (KI)^2.$$

Methylic sulphide boils at 41°. Its density is 0.845. It stands to methylic mercaptan in the same relation in which potassic sulphide ($K^2S$) stands to hydropotassic sulphide (HKS).

The addition of mercuric oxide precipitates the sulphur alcohol in combination with mercury in the form of the compound $\begin{pmatrix}(CH^3)^2\\Hg\end{pmatrix}S^2$, a white crystalline mass, which sulphurretted hydrogen decomposes—

$$H^2S + (CH^3)^2HgS^2 = HgS + \left(\begin{matrix}CH^3\\H\end{matrix}S\right)^2.$$

The compound $CH^4S$ is sometimes called methylic mercaptan, the name 'mercaptan' being given to the sulphur alcohols, from the force with which they react on mercuric oxide. They are remarkable for their peculiarly disagreeable smell.

**Mercaptan** $\left(\begin{matrix}C^2H^5\\H\end{matrix}S\right.$ = 2 vols.; boiling-point, 62°; sp. gr. $0.835\left.\right)$ is obtained by processes similar to those for obtaining the methylic compound. Mercaptan floats upon water, and is almost insoluble in it. At a low temperature it crystallizes. Nitric acid oxidizes it, forming hydrovinic sulphite $\left(\begin{matrix}C^2H^5\\H\end{matrix}SO^3\right)$.

Vinic sulphide ($(C^2H^5)^2S$ = 2 vols.; boiling-point, 73°; sp. gr. 0.825). When prepared by the action of vinic iodide on an alcoholic solution of potassic sulphide this compound can be precipitated from the alcoholic solution by the addition of water. It has an odour resembling that of garlic.

There is also a vinic disulphide, $(C^2H^5)^2S^2$.

**253. Amylic Mercaptan** $\left(\begin{matrix}C^5H^{11}\\H\end{matrix}S\right.$ = 2 vols.; boiling-point, 125°$\left.\right)$ and amylic sulphide ($(C^5H^{11})^2S$ = 2 vols.; boiling-

point, 216°) are made by processes similar to those adopted in the preparation of the methyle and ethyle compounds.

These compounds are analogous to the alcohols and ethers, and they are to be considered as derived from them by the substitution of an atom of sulphur for an atom of oxygen; the resulting sulphur compound occupying the same vapour-volume as the original oxygen compound. Vinic alcohol is decomposed by phosphoric sulphide, forming mercaptan, an atom of sulphur going into the place of the atom of oxygen in the alcohol; whereas when it is decomposed by phosphoric chloride, the atom of oxygen being replaced by two atoms of chlorine, the result is the formation of a molecule of vinic chloride plus a molecule of hydric chloride—

$$\begin{matrix} C^2H^5 \\ H \end{matrix} O + P Cl^5 = P O Cl^3 + C^2 H^5 Cl + H Cl.$$

If sulphur were monatomic, like chlorine, the phosphoric sulphide would form vinic sulphide and hydric sulphide in separate molecules, instead of the compound $\begin{matrix} C^2H^5 \\ H \end{matrix} S$.

The compounds containing ethyle, which are formed by the action of acids upon alcohol, are commonly called 'compound ethers,' and they are best classified according to the atomicity of the atoms from which they are formed. The simplest are those formed on the type of hydrochloric acid, each molecule occupying two volumes and containing one atom of ethyle, combined with one atom of an element analogous to chlorine, or one atom of a monatomic compound radical, such as $NO^3$, CN.

**254.** A considerable number of hydrocarbons are known containing more than twice as many atoms of hydrogen as of carbon. In composition they stand in the relation of homologues of marsh gas, but it is still an open question whether they should be ranged in one series as hydrides

of the radicals methyle, ethyle, propyle, &c., or whether some of them ought to be considered as containing two atoms homologous with methyle, united in one molecule. Thus a hydrocarbon consisting of $C^2H^6 = 2$ vols. has been obtained by the electrolysis of potassic acetate, in which process carbonic acid and a gas of this composition are given off at the positive pole, whilst hydrogen is evolved at the negative pole. When made in this manner the gas is called methyle, and its molecule is written thus—$(CH^3)^2$, while the systematic name 'methylic methide' is given to it. By the action of water on zinc ethyle a compound of identical composition is obtained, by the combination of hydrogen with ethyle, and when the gas is prepared in this way chemists call it ethylic hydride, and write its formula accordingly—$C^2H^5H$. A slight difference of solubility has been stated to distinguish the gas from the acetate from the gas made from zinc ethyle, and a difference in the products of the action of chlorine upon them; but there seems good reason to believe that the so-called methyle yields ethylic chloride among the products of the action of chlorine gas upon it. The gas ($C^4H^{10} = 2$ vols.) formed by the action of ethylic iodide on zinc ethide—

$$(C^2H^5I)^2 + Zn(C^2H^5)^2 = \begin{pmatrix} C^2H^5 \\ C^2H^5 \end{pmatrix}^2 + ZnI^2,$$

yielded by the action of chlorine a liquid of the composition $C^4H^9Cl$, which behaved like butylic chloride.

**255.** A hydrocarbon ($C^7H^{16} = 2$ vols.) was obtained by the action of sodium on a mixture of amylic iodide and ethylic iodide, and from the mode of its formation it was considered as built up of an atom of ethyle and an atom of amyle ($C^2H^5C^5H^{11}$). By the action of chlorine upon this compound two products were obtained besides hydrochloric acid. One of these compounds boiled at 150°, and was found to possess the composition and, at least, some of the properties of the chloride of the radical heptyl $C^7H^{15}Cl$.

The formation of marsh gas and its chief properties were described among the inorganic compounds of carbon, to which it may in some measure be considered to belong, from the fact that it is one of the most general products of the destructive distillation of organic bodies.

Berthelot has shewn that by the action of chlorine, marsh gas yields methylic chloride—

$$C H^4 + Cl^2 = C H^3 Cl + H Cl;$$

and that when heated with potassic hydrate this product forms potassic chloride and methylic alcohol—

$$C H^3 Cl + \begin{matrix} K \\ H \end{matrix} O = K Cl + \begin{matrix} C H^3 \\ H \end{matrix} O.$$

Marsh gas is obtained by the action of water on zinc methide—

$$H^2 O + (C H^3)^2 Zn = (C H^3 H)^2 + Zn O.$$

The next term of the series ($C^2 H^6$ = 2 vols.) is not only obtained by this process, as above mentioned, but also by the action of methylic iodide on zinc methide—

$$(C H^3 I)^2 + Zn (C H^3)^2 = (C^2 H^6)^2 + Zn I^2.$$

It has also been prepared by the action of potassium on vinic cyanide ($C^2 H^5 C N$), in which reaction it is accompanied by olefiant gas ($C^2 H^4$) and so-called ethyle ($C^4 H^{10}$).

The third term of the series is $C^3 H^8$ = 2 vols. It may be formed by uniting the radicals ethyle and methyle into one molecule ($C H^3 C^2 H^5$), or by combining the radical propyl with hydrogen.

The fourth term ($C^4 H^{10}$ = 2 vols.) is the gas usually called ethyle, and represented as containing in one molecule two atoms of that radical. It is isomeric with butylic hydride ($C^4 H^9 H$) and with propylic methide ($C^3 H^7 C H^3$).

At a pressure of 2.5 atmospheres ethyle condenses to a liquid at 3°C, and at the ordinary atmospheric pressure it requires a cold of − 23° for its liquefaction.

Some hydrocarbons have been built up partly from elements

supplied from one compound, partly by those supplied by another. Thus a hydrocarbon consisting of $C^7H^{16}$ = 2 vols., and considered as containing an atom of methyle united with an atom of caproyl $\left(\begin{matrix}C & H^3\\ C^6 & H^{13}\end{matrix}\right)$, has been formed by the electrolysis of a solution containing both potassic acetate ($K C^2H^3O^2$) and potassic caproate ($K C^7 H^{13} O^2$).

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# CHAPTER XL.

**256.** The chlorides of the alcohol radicals are obtained together with water by the action of hydrochloric acid on the alcohols—

$$\begin{matrix}CH^3\\ H\end{matrix} O + HCl = \begin{matrix}H\\ H\end{matrix} O + CH^3Cl.$$

Also by the action of an excess of phosphoric chloride on the alcohols, thus—

$$\begin{matrix}C^2H^5\\ H\end{matrix} O + PCl^5 = C^2H^5Cl + HCl + POCl^3.$$

Methylic chloride is also obtained by the action of iodic chloride on sodic acetate—

$$NaC^2H^3O^2 + Cl^2I^2 = NaCl + CH^3Cl + I^2 + CO^2.$$

The molecule of each of them occupies 2 volumes in the state of vapour. For the most part these chlorides are insoluble in water, but readily soluble in alcohol, ether, &c.

Methylic chloride dissolves however in water to a considerable extent, and forms with it a crystalline compound at 6°C.

**Vinic Chloride** boils at 11°C. It floats upon water, and dissolves very slightly in it. Its density at 5° is .874. Its

vapour has an agreeable odour, and burns with a bright flame, of which the borders are tinged with green.

Amylic chloride boils at 100°. The bromides of the alcohol radicals present great analogy with the chlorides both in their mode of formation, and in their properties and decompositions. One molecule of each of them occupies two volumes in the state of vapour. In the liquid state, as in the gaseous state, each of these bromides is heavier than the corresponding chloride. Thus ethylic bromide has a density of 1.4. Its vapour has a density of 54.5 (half its molecular weight), while the vapour-density of the chloride ($C^2H^5Cl$ = 2 vols.) is 32.25. The bromides boil at higher temperatures than the corresponding chlorides: thus vinic bromide ($C^2H^5Br$) boils at 41°C. Under the action of decomposing agents the bromides undergo double decompositions more easily than the chlorides.

**257.** Iodine forms a series of compounds with the alcohol radicals which are of great interest and value as reagents. They are perfectly analogous to the bromides and chlorides, but are far more easily decomposed, and are consequently more serviceable as affording means of replacing hydrogen or metals by the alcohol radicals. Their density and vapour-density are greater than those of the corresponding bromides. For instance, vinic iodide ($C^2H^5I$ = 2 vols.) has a density of 1.92 and a vapour-density of 78.

Methylic iodide ($CH^3I$ = 2 vols.; boiling-point, 43°; sp. gr. 2.2). This ether is easily obtained by the action of iodine and red phosphorus on methylic alcohol. It is also formed in considerable quantities by the action of hydriodic acid on narcotine. It has an agreeable, ethereal, and sweet odour. When exposed even to diffused light it becomes red from liberation of iodine. Its alcoholic solution precipitates silver nitrate rapidly—

$$CH^3I + AgNO^3 = CH^3NO^3 + AgI.$$

Ethylic iodide ($C^2H^5I$ = 2 vols.; boiling-point, 72°; sp. gr. 1.92) is obtained by the action of a mixture of iodine and phosphorous iodide on alcohol. It is decomposed by light, though less rapidly than the methylic iodide. A mixture of the three hydrocarbons $C^2H^4$, $C^2H^6$, and $C^4H^{10}$ is given off, while iodine dissolves in the liquid.

Amylic iodide ($C^5H^{11}I$ = 2 vols.) boils at 146°. Its density is only 1.51. In all its reactions this iodide manifests greater sluggishness than the ethyle compound; and the contrast is still greater with the methyle compound, which is the most decomposable of the whole series.

**258.** Side by side with these ethers should be studied the cyanides, such as methylic cyanide, vinic cyanide, &c. ($CH^3CN$, $C^2H^5CN$). These remarkable compounds have been made by two perfectly distinct processes: 1. By double decomposition between a methyle salt or double salt, and potassic cyanide. Thus methopotassic sulphate undergoes double decomposition with potassic cyanide, forming potassic sulphate and methylic cyanide—

$$\begin{matrix} CH^3 \\ K \end{matrix} SO^4 + KCN = K^2SO^4 + CH^3CN;$$

or better still, methylic iodide in presence of alcohol decomposes potassic cyanide—

$$CH^3I + KCN = CH^3CN + KI.$$

2. By the action of anhydrous phosphoric acid on ammonia acetate the elements of water are abstracted from the salt, and a volatile compound, originally called acetonitrile but found to be identical with methylic cyanide, is formed—

$$\begin{matrix} C^2H^3 \\ N\ H^4 \end{matrix} O^2 - (H^2O)^2 = CH^3CN.$$

Similar reactions occur with the higher terms of the acetic series; so that each cyanide can be made by uniting cyanogen with the alcohol radical or by deshydrating the ammonia

salt of an acid of the acetic series. Thus valeronitrile ($C^5H^{11}CN$) is made either from fousel oil or from ammonia caproate $\left(\begin{matrix}C^6H^{11}\\N\ H^4\end{matrix}O^2\right)$.

Under the action of a boiling solution of caustic potash these cyanides are decomposed, ammonia going off and a potash salt of the acetic series remaining behind. The acid of this salt contains the carbon of the alcohol radical added to the carbon of the cyanogen.

Thus methylic cyanide yields potassic acetate—

$$C^2H^3N + H^3KO^2 = C^2H^3KO^2 + NH^3.$$

Ethylic cyanide gives rise in this manner to potassic propionate—

$$C^3H^5N + H^3KO^2 = C^3H^5KO^2 + NH^3.$$

Methylic cyanide is a fragrant liquid, which floats upon water and boils at 77°. All the terms of this series occupy two volumes in the shape of vapour.

**259.** The cyanates—such as **Methylic Cyanate** ($CH^3CNO$), **Vinic Cyanate** ($C^2H^5CNO$), are formed by heating an intimate mixture of potassic cyanate with a double sulphate containing an alcohol radical and potassium. Thus methylic cyanate is obtained by distilling a mixture of potassic cyanate and methopotassic sulphate—

$$KCNO + \begin{matrix}CH^3\\K\end{matrix}SO^4 = CH^3CNO + K^2SO^4.$$

Vinic cyanate is obtained by a similar process, using ethylopotassic sulphate. This cyanate is a liquid of exceedingly pungent odour. It boils at 60°C. Ethylic cyanurate is formed at the same time and crystallizes out from the cyanate. Its composition corresponds to that of metallic cyanurate, being $(C^2H^5)^3C^3N^3O^3$.

When either of these ethers is boiled with caustic potash a decomposition occurs, forming potassic carbonate and a kind

of ammonia containing an atom of ethyle (or methyle) and two atoms of hydrogen united with an atom of nitrogen—

$$C^2H^5NCO + H^2K^2O^2 = K^2CO^3 + C^2H^5H^2N.$$

This remarkable base was called ethylamine by Wurtz, its discoverer. It was the first of an immense family of ammonias containing organic radicals in the place of some of the hydrogen of common ammonia. Methylic cyanate yields, when acted upon by potassic hydrate, a volatile base, called methylamine, and containing $CH^5N$. In like manner amylamine is obtained from amylic cyanate. Ethylic cyanate combines with ammonia, forming a compound called ethylurea, being a molecule of urea in which an atom of hydrogen is replaced by ethyle—

$$C^2H^5CNO + NH^3 = CN^2H^3(C^2H^5)O.$$

Common urea is $CN^2H^4O$.

The sulphocyanates of the alcohol radicals correspond in their mode of formation and in their composition to the cyanates, containing an atom of sulphur in lieu of the atom of oxygen. Thus ethylic sulphocyanate ($C^2H^5CNS$ = 2 vols.) is obtained by distilling a mixture of potassic sulphocyanate and ethylopotassic sulphate in concentrated aqueous solution—

$$KCNS + C^2H^5KSO^4 = C^2H^5CNS + K^2SO^4;$$

it sinks to the bottom of water, and boils at 146°. By the action of potassic hydrate it has not been found to yield ethylamine.

**260.** There are ethers corresponding to monatomic nitrites and nitrates. By the action of nitric acid on an alcohol a mixture of products of oxidation of the alcohol with a nitrite is usually obtained, and for the preparation of the pure nitrites it is found most advantageous to mix the alcohol with nitric acid in the cold and to add copper turnings to the mixture.

Methylic nitrite ($CH^3NO^2$), obtained in this manner from methylic alcohol, is a liquid which boils below 0°. It is

formed by the action of nitric acid on brucia. Vinic nitrite ($C^2 H^5 N O^2$ = 2 vols.), or nitrous ether, should be made to pass from the flask in which it is generated, through a bottle of water, and then through a tube full of calcic chloride. It condenses to a liquid which boils at about 21°, and has an exceedingly fragrant agreeable odour.

It was discovered by Millon that the presence of urea in a mixture of alcohol and nitric acid prevents the oxidizing action which otherwise takes place upon the alcohol, and consequently prevents the formation of a nitrite. Ethylic nitrate ($C^2 H^5 N O^3$), obtained in this manner, is a liquid heavier than water and quite insoluble in it. The nitrate boils at 85°, and its vapour explodes with violence when much superheated.

**261.** The **Alcoholic Carbonates** are of two classes. 1. Normal carbonates, such as vinic carbonate ($(C^2 H^5)^2 C O^3$ = 2 vols.) These salts are most easily obtained by the action of metallic sodium on a corresponding oxalate. Each molecule of these ethers contains two atoms of the alcohol radical and occupies the same vapour-volume as one molecule of chloride, bromide, &c. 2. Double carbonates, such as hydrovinic carbonate ($H C^2 H^5 C O^3$), called carbovinic acid from the facility with which its typical hydrogen can be replaced by potassium, sodium, &c., forming salts, such as ethylopotassic carbonate ($C^2 H^5 K C O^3$), &c., or by an alcohol radical, as in the case of vinomethylic carbonate—

$$C^2 H^5 C H^3 C O^3.$$

Strong alcohol, in which potassic hydrate has been dissolved, contains potassic ethylate ($K C^2 H^5 O$), and accordingly carbonic acid passed into the liquid forms vinopotassic carbonate by uniting with the ethylate. A good deal of potassic carbonate is formed at the same time, but being insoluble in alcohol, this salt goes down, whilst the double salt remains in part at least in the liquid, from which it can be

precipitated by the addition of ether. It can be purified by solution in dry alcohol and re-precipitation by ether.

The sulphur salts corresponding to these carbonates are easily obtained by corresponding processes.

Thus vinic sulphocarbonate ($(C^2H^5)^2CS^3$) is formed by the action of vinic chloride on the double salt $C^2H^5KCS^3$, and this double salt is obtained by pouring carbonic sulphide into an alcoholic solution of potassic sulphide, which no doubt contains ethylopotassic sulphide ($C^2H^5KS$).

**262.** The **Alcoholic Oxalates** are, like the carbonates, of two classes—viz. normal oxalates, such as vinic oxalate ($(C^2H^5)^2C^2O^4$), which contain two atoms of the alcohol radical in each volume while occupying the normal molecular volume. There are also double oxalates, such as hydrovinic oxalate ($HC^2H^5C^2O^4$), vinopotassic oxalate ($C^2H^5KC^2O^4$), ethylomethylic oxalate ($C^2H^5CH^3CO^4$).

**Vinic Oxalate** ($(C^2H^5)^2C^2O^4 = 2$ vols.; boiling-point, 182°; sp. gr. 1.1) is formed by passing hydrochloric acid gas into a mixture of dry alcohol and oxalic acid, or by heating the mixture with sulphuric acid. In either case the mineral acid accelerates a process which takes place more slowly without its intervention. The ether is almost insoluble in water.

Its solution in alcohol is decomposed by the cautious addition of potash, with formation of a precipitate of vinopotassic oxalate ($C^2H^5KC^2O^4$), whilst alcohol is formed. Ammonia decomposes the ether rapidly, forming oxamide and alcohol—

$$(C^2H^5)^2C^2O^4 + (NH^3)^2 = N^2H^4C^2O^2 + (HC^2H^5O)^2.$$

By the cautious addition of an alcoholic solution of ammonia to a similar solution of the ether, an intermediate compound is formed, consisting of crystalline plates possessing the composition

$$C^2H^5NH^2C^2O^3 = (C^2H^5)^2C^2O^4 + NH^3 - HC^2H^5O.$$

This compound is considered as an oxamate.

Oxalic ether is gradually decomposed by cold water, but more rapidly by boiling water, the ultimate products being alcohol and water. Its formation and subsequent decomposition afford the best means of obtaining oxalic acid free from mineral impurity, as the ether is easily purified by distillation.

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# CHAPTER XLI.

**263.** Sulphurous acid forms a normal ethyle salt, which is obtainable by the action of hyposulphurous chloride on absolute alcohol. It is a colourless liquid, somewhat heavier than water, and nearly insoluble in it. Its molecule occupies the normal volume, and contains two atoms of ethyle ($(C^2H^5)^2SO^3$ = 2 vols.) It boils at 160°C.

Hydrovinic sulphite ($HC^2H^5SO^3$) is formed by the action of nitric acid on mercaptan. It can be obtained in the form of crystals from a concentrated aqueous solution. Its salts, even with barium and lead, are soluble in water.

**264. Vinic Sulphate** ($(C^2H^5)^2SO^4$) is formed by slowly passing the vapour of anhydrous sulphuric acid into ether cooled by immersion in a frigorific mixture. The product is shaken up with a mixture of ether and water, the sulphate being dissolved by the former, while various foreign bodies are dissolved by the water. The sulphate is obtained by evaporation of its ethereal solution. It cannot be distilled without decomposition.

Far more important are the double sulphates containing ethyle and metals, the so-called sulphovinates. Sulphovinic

acid is formed simultaneously with water by mixing alcohol and strong sulphuric acid—

$$\begin{matrix} C^2H^5 \\ H \end{matrix} O + \begin{matrix} H \\ H \end{matrix} S O^4 = \begin{matrix} C^2H^5 \\ H \end{matrix} S O^4 + \begin{matrix} H \\ H \end{matrix} O.$$

The mixture after standing for some days, or after heating, should be poured in a fine stream into an excess of slaked lime suspended in water with lumps of ice, and the mass should be constantly agitated while the acid mixture flows into it. Calcic sulphate and sulphovinate are formed, and the latter being readily soluble in water is separated by filtration, and crystallized from its solution by evaporation. The salt crystallizes in plates, which contain two molecules of water of crystallization—

$$Ca\,(C^2H^5)^2\,(S O^4)^2\,(H^2O)^2.$$

The solution of this or of any metallic sulphovinate can be heated in presence of water without undergoing decomposition; but when the fixed base is replaced by hydrogen, by the addition of hydrochloric or sulphuric acid, the double sulphate decomposes easily, alcohol and a sulphate being formed. Thus an aqueous solution of barytic sulphovinate deposits barytic sulphate when boiled with hydrochloric acid—

I. $$\begin{matrix} (C^2H^5)^2 \\ Ba \end{matrix} (S O^4)^2 + H^2 Cl^2 = \left(\begin{matrix} C^2H^5 \\ H \end{matrix} S O^4\right)^2 + Ba\,Cl^2;$$

II. $$\begin{matrix} C^2H^5 \\ H \end{matrix} S O^4 + \begin{matrix} H \\ H \end{matrix} O = \begin{matrix} H \\ H \end{matrix} S O^4 + \begin{matrix} C^2H^5 \\ H \end{matrix} O;$$

III. $$H^2 S O^4 + Ba\,Cl^2 = Ba\,S O^4 + (H\,Cl)^2.$$

The other alcohol radicals form similar double sulphates. Thus we have the sulphomethylates, such as potassic sulphomethylate ($K C H^3 S O^4$), barytic sulphomethylate ($Ba\,(C H^3)^2\,(S O^4)^2$), &c. Also the corresponding sulphoamylates ($K C^5 H^{11} S O^4$, $Ba\,(C^5 H^{11})^2\,(S O^4)^2$), &c.

The same difference which was pointed out between the iodides of these radicals, in respect to the rapidity with which they exchange their radicals for metals, in processes

of double decomposition, holds good with regard to these double sulphates. The sulphomethylates are far more rapidly decomposed than the sulphovinates, and the sulphoamylates far less rapidly.

**265.** Side by side with these salts, containing biatomic radicals, may be considered compounds of the dyads zinc and mercury with the radicals. These compounds are of two classes: one class consisting of compounds of an atom of metal with two atoms of alcohol radical, such as $Zn\,(C\,H^3)^2$, $Hg\,(C^2\,H^5)^2$, &c.; the other class consisting of compounds of one atom of metal and one atom of chlorine or iodine, &c., such as $Zn\,C\,H^3\,I$, $Hg\,C\,H^3\,I$, &c. The latter class must be considered as double salts, in which the alcohol radical has chlorous functions. The compounds belonging to it may be compared to the inorganic salts of the corresponding metals, such as $Zn\,Cl^2$, $Hg\,I^2$, &c., one atom of the chlorous constituent of these being replaced by an atom of alcohol radical. They are formed by the action of the metals on the corresponding ethers. Thus zinc combines with methylic iodide at the ordinary temperature, forming zinc methiodide ($Zn\,Me\,I$), ($Me = C\,H^3$). The best way to obtain the compound is to use zinc amalgam, containing 12 to 15 per cent. of mercury, and in the state of fine powder. In a glass bottle the combination is complete after contact of two or three weeks at the ordinary temperature, when enough amalgam is used to fill the liquid; but it is complete in a few hours if the same mixture be heated to 100° in an iron digestor.

The compound consists of scaly crystals, which are easily decomposed by distillation, even in vacuo.

The products are zinc methide, which distils over, and zinc iodide, which remains behind—

$$(Zn\,C\,H^3\,I)^2 = Zn\,(C\,H^3)^2 + Zn\,I^2.$$

Zinc methiodide emits dense white fumes in contact with

moist air. It is decomposed with great violence by water, marsh gas being evolved.

Zinc ethiodide ($Zn\,C^2\,H^5\,I$) is formed in the same way as the methyle compound, but it requires longer contact of the metal and iodide. It is also decomposed by distillation into zinc iodide and zinc ethide.

Zinc ethide and zinc methide are liquids heavier than water. They catch fire spontaneously in contact with air, but when oxygen is brought gradually in contact with the ethide zinc alcohol is formed $\left(\begin{matrix}(C^2H^5)^2\\Zn\end{matrix}O^2\right)$.

Zinc ethide occupies two volumes in the state of vapour ($Zn\,(C^2H^5)^2 = 2$ vols.), the two atoms of ethyle being held together by one atom of zinc. The compound boils at 110°.

Ammonia gas decomposes it, forming zinc amide and ethylic hydride; $Zn\,(C^2H^5)^2 + (N\,H^3)^2 = Zn\,(N\,H^2)^2 + (C^2\,H^6)^2$.

Potassium decomposes zinc ethide, forming a solution of potassic ethide in the zinc compound—

$$Zn\,(C^2\,H^5)^2 + K^2 = (K\,C^2\,H^5)^2 + Zn.$$

By heating zinc ethide with ethylic iodide Frankland obtained the so-called ethyle or ethylic ethylide—

$$Zn\,(C^2\,H^5)^2 + (C^2\,H^5\,I)^2 = Zn\,I^2 + (C^4\,H^{10})^2;$$

and in like manner ethylic methylide is formed by the action of zinc ethide on methylic iodide—

$$Zn\,(C^2\,H^5)^2 + (C\,H^3\,I)^2 = Zn\,I^2 + (C^3\,H^8)^2.$$

**266. Mercuric Methiodide** ($Hg\,C\,H^3\,I$) is formed by exposing metallic mercury and methylic iodide to the sunshine, with frequent agitation. It crystallizes in scales, which can easily be volatilized without decomposition. The iodine can be replaced in this compound by an equivalent quantity of a monatomic radical, or even of a diatomic or triatomic radical, forming salts such as—

$$Hg\begin{matrix}C\,H^3\\N\,O^3\end{matrix},\quad Hg^2\begin{matrix}(C\,H^3)^2\\S\,O^4\end{matrix},\quad Hg^3\begin{matrix}(C\,H^3)^3\\P\,O^4\end{matrix},\quad \&c.$$

The mercuric ethiodide is not easily obtained in quantity by combination of the metal with ethylic iodide. It is best obtained by combination of mercuric iodide and mercuric ethide—

$$Hg\,I^2 + Hg\,(C^2H^5)^2 = (Hg\,C^2H^5I)^2.$$

Mercuric methide is easily obtained by Frankland and Duppa's process of acting on ethylic iodide in presence of a little acetic ether by a very weak sodium amalgam.

Mercuric methide is not decomposed by alcoholic potash. Hydrobromic acid decomposes it, evolving marsh gas, and forming mercuric methylobromide—

$$Hg\,(CH^3)^2 + Br\,H = Hg\begin{matrix}CH^3\\Br\end{matrix} + CH^4.$$

Bromine forms methylic bromide, and the methylobromide—

$$Hg\,(CH^3)^2 + Br^2 = Hg\begin{matrix}CH^3\\Br\end{matrix} + CH^3\,Br.$$

These compounds are not decomposed by water.

The molecule of each of them occupies in the state of vapour two volumes.

Mercuric methide has a density of 3.069, and boils at 93 to 96°. Mercuric ethide has a density of 2.46, and boils at 159°. Both compounds are decomposed by metallic zinc, or by metallic aluminium.

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# CHAPTER XLII.

**267.** The compounds formed by the alcohol radicals with triatomic salt radicals correspond in their mode of formation and in their general properties to the other salts. Thus, there are three phosphates—

$(C^2H^5)^3\,P\,O^4$, $H\,(C^2H^5)^2\,P\,O^4$, and $H^2\,(C^2H^5)\,P\,O^4$.

The typical hydrogen in the last two is replaceable by basylous metals, forming salts, such as the diethylosodic phosphate $(C^2H^5)^2NaPo^4$, &c. There are also similar phosphites, such as $(C^2H^5)^3Po^3$, &c. Thus, vinic phosphite is obtained by the action of phosphorous chloride on sodic ethylate—

$$P Cl^3 + \left(\begin{matrix}C^2H^5\\Na\end{matrix}O\right)^3 = (Na\,Cl)^3 + \begin{matrix}(C^2H^5)^3\\P\end{matrix}O^3.$$

It is thus formed from three molecules of alcohol, which are held together by the triad phosphorus replacing one atom of hydrogen in each molecule. Vinic phosphate may similarly be represented as containing the triatomic radical PO in the place of the atoms of hydrogen from three molecules of alcohol; $\begin{matrix}(C^2H^5)^3\\PO\end{matrix}O^3$.

Vinic borate ($(C^2H^5)^3BO^3$ = 2 vols.; boiling-point, 119°) is formed by the action of boric chloride on alcohol—

$$B Cl^3 + \begin{matrix}(C^2H^5)^3\\H^3\end{matrix}O^3 = (Cl\,H)^3 + \begin{matrix}(C^2H^5)^3\\B\end{matrix}O^3.$$

Zinc ethide desoxidizes this ether completely, forming boric ethide ($B(C^2H^5)^3$).

By the action of chloroform on sodic ethylate a compound has been obtained, consisting of $\begin{matrix}(C^2H^5)^3\\CH\end{matrix}O^3$ = 2 vols.

By the action of hydrochloric acid it is decomposed, forming ethylic formiate, $\begin{matrix}C^2H^5\\C\ H\end{matrix}O^2$, and ether, $(C^2H^5)^2O$.

**268.** Amongst the most remarkable of compounds containing the alcohol radicals are the bases analogous to ammonia, but containing ethyle or methyle, &c., in the place of one or more atoms of hydrogen of ammonia.

**Methylamine** ($CH^3HHN$) was mentioned above as formed by the action of nascent hydrogen on prussic acid. It was first obtained by the action of caustic potash on

*methylic* cyanate. Ethylamine ($C^2H^5HHN$) and amylamine ($C^5H^{11}HHN$) were obtained in like manner from the corresponding cyanates.

**Ethylamine** can also be prepared by the action of ammonia on ethylic bromide. A direct combination takes place when the substances are heated together under pressure, forming ethylaminic bromide ($NHHC^2H^5HBr$); and when this salt is distilled with caustic potash, ethylamine goes over.

Ethylamine can be condensed to a liquid which boils at 18.7°. Its density at 8° was found to be 0.696.

In the state of vapour its molecule occupies 2 volumes ($C^2H^7N$ = 2 vols.) Its vapour-density is therefore 22.5.

It combines with acid hydrogen salts in the same manner as ammonia combines with them, forming compounds such as $NH^3C^2H^5Cl$, $(NC^2H^8)^2SO^4$, &c. It precipitates the heavy metallic oxides from solutions of their salts, and dissolves cupric oxide. It differs from ammonia by dissolving alumina, when added in excess to a solution of a salt of that base. Its hydrochlorate combines with platinic chloride in the same proportion as ammonia chloride combines with it; but the double chloride $PtCl^6N^2C^4H^{16}$ is more soluble in water than the compound formed from ammonia.

**269. Diethylia** ($(C^2H^5)^2HN$ = 2 vols.; boiling-point, 57°) can be obtained from ethylamine by the action of ethylic bromide and subsequent distillation with potash. It resembles ethylamine very much in its reactions, but when the two bases are mixed with one another they can be separated by the action of oxalic ether, which forms with diethylia the compound called diethyloxamic ether, which is insoluble in water; whereas ethylamine forms under like circumstances diethyloxamide, a crystalline body which dissolves in water. Both of these compounds are decomposed by boiling potash; the one yielding ethylamine, the other diethylia.

**Triethylia** ($(C^2H^5)^3N$ = 2 vols.) is formed from diethylia by the further action of ethylic bromide. Triethylia combines in its turn with ethylic bromide, or still better with ethylic iodide ($N(C^2H^5)^3C^2H^5I = N(C^2H^5)^4I$). The salt thus formed contains **Tetrethylammonium** ($N(C^2H^5)^4$), and other salts can be prepared from it by processes of double decomposition. Thus a solution of the iodide shaken up with freshly-precipitated silver hydrate, forms silver iodide and tetrethylammonium hydrate—

$$N(C^2H^5)^4I + \begin{matrix}Ag\\H\end{matrix}O = AgI + \begin{matrix}N(C^2H^5)^4\\H\end{matrix}O.$$

This remarkable base is best described by comparison with potash, which it resembles in its strongly caustic properties. It is decomposed by distillation, yielding triethylia, ethylene, and water—

$$N(C^2H^5)^4HO = N(C^2H^5)^3 + C^2H^4 + H^2O.$$

The corresponding compound made from methyle breaks up on distillation, yielding trimethylia and methylic alcohol—

$$N(CH^3)^4HO = N(CH^3)^3 + CH^4O.$$

When ammonia is heated with ethylic iodide a mixture is obtained of the five salts, $NH^4I$, $NC^2H^8I$, $NC^4H^{12}I$, $NC^6H^{16}I$, and $NC^8H^{20}I$. By distilling the mixture with potash a mixture of ammonia with ethylamine, diethylia, and triethylia is obtained. The last three of these are separated by the action of oxalic ether, for triethylia does not react on the ether, and can be distilled off by the heat of the water-bath, together with the alcohol formed in the reaction, from the diethyloxamide and diethyloxamic ether. On the separation of these two by water, as above described, the diethyloxamic ether is accompanied by oxamide, but the ammonia evolved by the decomposition of the oxamide can easily be separated from the triethylia.

Not only can the three atoms of hydrogen in ammonia be replaced one after another by atoms of ethyle, or methyle,

or amyle, &c., but they may be replaced by different radicals. Thus an ammonia may be made containing the three radicals methyle, ethyle, and amyle, in one molecule—

$$N C H^3 C^2 H^5 C^5 H^{11};$$

and this ammonia can be combined with the iodide of a fourth radical if desired, such as propylic iodide, thus forming an ammonium iodide, each of whose four atoms of hydrogen is replaced by a distinct alcohol radical. Such a salt would of course have a long name, as much has to be said about it. For instance, the salt $N C H^3 C^2 H^5 C^3 H^7 C^4 H^9 I$ might have to be called am-meth-eth-pro-ammonium iodide.

**270.** Similar bases to these have been prepared with phosphorus instead of nitrogen. Zinc ethide combines with phosphorous chloride, and the compound

$$(Zn (C^2 H^5)^2)^3 + (P Cl^3)^2 = (Zn Cl^2)^3 (P (C^2 H^5)^3)^2$$

yields on distillation with caustic potash a base containing in each molecule one atom of phosphorus combined with three atoms of ethyle ($P (C^2 H^5)^3$ = 2 vols.) This body catches fire spontaneously in the air. It combines rapidly with vinic or methylic iodide, forming iodides of phosphorus ammoniums. It is insoluble in water, and has a density of 0.812. It boils at 127°.

It combines with oxygen, sulphur, iodine, &c., forming bodies such as $P (C^2 H^5)^3 O$, $P (C^2 H^5)^3 S$, $P (C^2 H^5)^3 I^2$, &c.

There seems to be another compound of phosphorus with ethyle of the composition $P^2 (C^2 H^5)^4$.

**271.** Arsenic has long been known to form a compound with methyle of which the oxide is formed by distillation of arsenious acid with potassic acetate—

$$As^2 O^3 + (C^2 H^3 K O^2)^4 = \frac{As (C H^3)^2}{As (C H^3)^2} O + (K^2 C O^3)^2 + (C O^2)^2.$$

This monatomic radical ($As (C H^3)^2$) is called **Kakodyle.** Its compounds were admirably investigated many years ago by Bunsen, and kakodyle was the first well-made-out instance

of an organic radical. Even to this day it continues to be one of the best made-out cases of that important class of bodies.

The oxide $(As(CH^3)^2)^2O$, kakodylic oxide, is very slightly soluble in water. It is a liquid boiling at about 120°C. Hydrochloric acid dissolves it, forming the chloride $As(CH^3)^2Cl$ and water—

$$(As(CH^3)^2)^2O + (HCl)^2 + (As(CH^3)^2Cl)^2 + H^2O.$$

Hydrobromic and hydriodic acids act in like manner. Metallic zinc heated with dry kakodylic chloride liberates the radical kakodyle $(As(CH^3)^2)^2$. There is reason to believe that free kakodyle is part at least of the product obtained in the distillation of arsenious acid and an acetate. The radical absorbs oxygen with great avidity, and catches fire spontaneously in the air. It forms a dioxide, $(As(CH^3)^2)^2O^2$, and an acid, $As(CH^3)^2\frac{O}{H}O$. It also forms a sulphide,

$$(As(CH^3)^2)^2S,$$

and a cyanide, $As(CH^3)^2CN$.

**272.** The various compounds containing arsenic in combination with ethyle or methyle and salt radicals, are best arranged in the types $AsCl^3$ and $As(CH^3)^4Cl$, the arsenic being triatomic in the one class of compounds and pentatomic in the other. The first may be called the ammonia type, the second the ammonium-chloride type. In the ammonia type are the compounds—

| | |
|---|---|
| $As(CH^3)^2Cl$. | $AsCH^3Cl^2$. |
| $As(CH^3)^2Br$. | $AsCH^3Br^2$. |
| $As(CH^3)^2I$. | $AsCH^3I^2$. |
| $As(CH^3)^2CN$. | $AsCH^3O$. |
| $As(C^2H^5)^2I$. | $AsCH^3S$. |
| $As(C^2H^5)^2HO$. | |

In the ammonium-chloride type are such compounds as—

| | | |
|---|---|---|
| $As(C^2H^5)^4Cl$. | $As(C^2H^5)^3I^2$. | $As(CH^3)Cl^4$. |
| $As(C^2H^5)^4Br$. | $As\ C^2H^5)^3O$. | $As(CH^3)^4As$. |
| $As(C^2H^5)^4I$. | $As(C^2H^5)^3S$. | $As(C^2H^5)^4As$. |
| $As(C^2H^5)^3Br^2$. | $As(CH^3)^2Cl^3$. | |

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# CHAPTER XLIII.

**273.** Antimony also combines with the alcohol radicals, forming compounds in the ammonia type. Such are stibethyle ($Sb(C^2H^5)^3$), stibmethyle ($Sb(CH^3)^3$). These compounds have been obtained by the action of sodic stibide on ethylic or methylic iodide. But they are better obtained by the action of antimonious chloride on zinc ethide or methide. They combine with oxygen, forming compounds in the ammonium chloride type, such as $Sb(C^2H^5)^3O$. It is even said that stibethyle decomposes hydrochloric acid with evolution of hydrogen—

$$Sb(C^2H^5)^3 + (HCl)^2 = Sb(C^2H^5)^3Cl^2 + H^2.$$

Bismuth also forms organic compounds in the ammonia type, such as $Bi(C^2H^5)^3$ and $Bi(C^2H^5)Cl^2$, but they are not volatile without decomposition.

Aluminic methide and ethide have been formed by the action of aluminium on zinc methide or ethide. At temperatures moderately above its boiling-point the former was found to occupy the normal volume $Al^2(CH^3)^6$ = 2 vols., but at a higher temperature it yielded nearly four volumes.

**274.** With tetratomic salt radicals the alcohol radicals

form salts, of which each molecule contains four atoms of the alcohol radical. Thus the phosphate $Ag^4P^2O^7$ is decomposed by ethylic iodide, forming $(C^2H^5)^4P^2O^7$.

Silicic chloride, by acting on absolute alcohol, forms an ether containing one atom of silicon in the place of the four typical atoms of hydrogen of four molecules of alcohol, $\underset{Si}{(C^2H^5)^4}O^4$. This remarkable body is insoluble in water, but is gradually decomposed by contact with it into gelatinous silica and alcohol. It boils without decomposition at 165°, and its vapour has the density 146, corresponding to $C^8H^{20}SiO^4$ = 2 vols. Another silicic ether containing only two atoms of ethyle in each molecule has been described— $\underset{Si}{(C^2H^5)^2}O^3$; boiling-point, 360°. A hexatomic compound, $\underset{Si^2}{(C^2H^5)^6}O^7$, intermediate between the last two, has also been described.

This hexethylic disilicate is formed by the removal of the elements of a molecule of ether from two molecules of the normal silicate—

$$((C^2H^5)^4SiO^4)^2 - (C^2H^5)^2O = (C^2H^5)^6P^2O^7,$$

just as so-called sodic pyrophosphate is formed from two molecules of hydrodisodic phosphate by the removal of $H^2O$—

$$(HNa^2PO^4)^2 - H^2O = Na^4P^2O^7.$$

Ethylic silicide ($Si(C^2H^5)^4$ = 2 vols.) has been obtained by the action of zinc ethide on silicic chloride. The compound is lighter than water, and boils without decomposition between 152° and 154°. It is not attacked either by nitric acid or by potash.

Tin forms with the alcohol radicals a variety of compounds belonging to the type of marsh gas. They are obtained by the action of sodic stannide on the iodides of the radicals. When the stannide is rich in sodium the tin combines with

four atoms of the alcohol radical, but when a less energetic alloy is used, one or more of the four atoms is iodine in lieu of the organic radical.

Thus there are stannic ethide ($Sn(C^2H^5)^4 = 2$ vols.), stannic methide ($Sn(CH^3)^4 = 2$ vols.), &c.; also stannic trimethyl iodide ($Sn(CH^3)^3I$), and chloride, &c.; stannic diethyl iodide ($Sn(C^2H^5)^2I^2$), or nitrate—

$$Sn(C^2H^5)^2(NO^3)^2.$$

**Plumbic Ethide** or methide are obtained by the action of plumbic chloride ($PbCl^2$) on the zinc ethide or methide. The mass becomes black from the liberation of finely-divided metallic lead; and on distilling it at a reduced pressure, a compound of lead with four atoms of the organic radical is separated out from it. Plumbic ethide ($Pb(C^2H^5)^4$) boils at about 200°. By the action of hydrochloric acid on plumbic ethide a plumbic triethochloride is obtained, with evolution of ethylic hydride—

$$Pb(C^2H^5)^4 + HCl = Pb(C^2H^5)^3Cl + C^2H^6.$$

A plumbethylic sulphate corresponding to this chloride has also been obtained. Its formula is $(Pb(C^2H^5)^3)^2SO^4$.

**275.** Besides the alcohols homologous with vinic alcohol others have been obtained, containing monatomic hydrocarbon radicals with a smaller proportion of hydrogen. Thus the heavy oil ($C^3H^5I$) formed by the action of phosphorous iodide on glycerine, has been found to react in many respects like ethylic iodide. With silver oxalate it forms silver iodide and a liquid of the composition $(C^3H^5)^2C^2O^4$, which behaves as an oxalate containing the radical allyl $C^3H^5$ as a base. Ammonia gas decomposes this oxalate, forming oxamide and allylic alcohol, $\begin{matrix}C^3H^5\\H\end{matrix}O$, a liquid boiling at 103°—

$$(C^3H^5)^2C^2O^4 + (NH^3)^2 = (NH^2)^2C^2O^2 + (C^3H^6O)^2.$$

By the action of potassium on this alcohol the compound

$C^3H^5KO$ was obtained; and allylic iodide replaces the potassium by allyl, forming allylic ether—

$$\begin{matrix} C^3H^5 \\ C^3H^5 \end{matrix} O;$$ boiling-point, 82°.

Allylic sulphide ($C^6H^{10}S$) has also been prepared, and found to be identical with the essential oil of garlic.

Allylic sulphocyanate ($C^3H^5CNS$) is obtained by the action of allylic iodide on potassic sulphocyanate. It is identical with the essential oil of mustard.

**276.** An exceedingly important body, which in its general properties must be classed among the monatomic alcohols, is the crystallizable principle of coal-tar creosote.

**Phenilic Hydrate** ($C^6H^6O$; boiling-point, 188°). Pure coal-tar creosote consists chiefly of this compound, and by fractional distillations it is separated from the moisture and cresylic hydrate which accompany it. It crystallizes in needles, which melt at 35°.

Phenilic alcohol is very slightly soluble in water, but sufficiently so to impart to it the peculiar odour of creosote, and the property for which the alcohol is remarkable—of arresting putrefaction or fermentation. The alcohol dissolves in aqueous potash, forming the compound $\begin{matrix} C^6H^5 \\ K \end{matrix} O$ (potassic phenylate). Strong sulphuric acid also dissolves it, forming sulphophenilic acid, $\begin{matrix} C^6H^5 \\ H \end{matrix} SO^4$, analogous to sulphovinic acid.

Chlorine acts very violently upon phenilic alcohol, forming hydrochloric acid and products of substitution of chlorine for the hydrogen of the alcohol, such as the so-called dichlorophenilic acid, $\begin{matrix} C^6Cl^2H^3 \\ H \end{matrix} O$, or the trichlorophenilic acid, $\begin{matrix} C^6Cl^3H^2 \\ H \end{matrix} O$, &c. Bromine acts in like manner.

The action of nitric acid on phenilic alcohol is exceedingly

energetic. It consists in forming water, and replacing the hydrogen in the alcohol, atom for atom, by $NO^2$. The most important of the products thus obtained is the trinitrophenilic or carbazotic acid, $\begin{matrix} C^6H^2(NO^2)^3 \\ H \end{matrix} O$, a compound which has been obtained not only by this process, but also by the action of nitric acid on indigo and a great number of other organic bodies.

**Carbazotic Acid** crystallizes from water in bright yellow crystals. Its potassium salt ($C^6H^2(NO)^3KO$) is very slightly soluble in water. The acid is used as a yellow dye. Nitrophenilic acid ($C^6H^5NO^2O$) and dinitrophenilic acid ($C^6H^4(NO^2)^2O$) have also been obtained.

There is no doubt that these various products of substitution formed from phenilic alcohol by the replacement of part of its hydrogen by chlorine or chlorous atoms, such as $NO^2$, must be stronger acids than the phenilic hydrate.

Phosphoric chloride forms phenilic phosphate $(C^6H^5)^3PO^4$, and at the same time phenilic chloride ($C^6H^5Cl$) by its action on the alcohol.

Phosphorous chloride forms among other products the hydrocarbon $C^6H^6$, called benzole.

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# CHAPTER XLIV.

**277. Benzole.** This important hydrocarbon was discovered by Faraday in coal-gas, and is now manufactured in large quantities from the neutral oil of coal-tar. It was also

obtained by Mitscherlich by distilling an alkaline benzoate with an alkaline hydrate. Thus—

$$C^7H^5NaO^2 + HNaO = C^6H^6 + Na^2CO^3.$$

This reaction shews it to stand to benzoic acid in the same relation in which marsh-gas stands to acetic acid. When contaminated with a small quantity of the other oils which occur with it in coal-tar, benzole can be purified by crystallization by the aid of artificial cold. The crystals of benzole which are obtained should be rapidly pressed, so as to remove the liquid oils adhering to them. In this manner it is obtained in the form of a colourless mobile liquid of 0.85, sp. gr. at 15.5°C. It has a sweetish and not disagreeable smell. It freezes at 5.5°, and boils at 80°. Its vapour-density is 39.

Benzole ($C^6H^6$ = 2 vols.) is soluble in water. It dissolves fats very readily, as well as india-rubber and gutta-percha. Strong sulphuric acid dissolves benzole with the aid of heat, forming an acid of the composition $\begin{matrix} C^6H^5 \\ H \end{matrix} SO^3$, which may be called sulphiphenilic acid, from its analogy with sulphivinic acid, $\begin{matrix} C^2H^5 \\ H \end{matrix} SO^3$.

Strong nitric acid transforms benzole into a fragant oil called **Nitrobenzole.** This compound is heavier than water, and has the composition $C^6H^5NO^2$. The reaction is an interchange between H in the oil and $NO^2$ in the acid—

$$C^6H^6 + \begin{matrix} H \\ NO^2 \end{matrix} O = C^6H^5NO^2 + \begin{matrix} H \\ H \end{matrix} O.$$

Strong nitric acid, mixed with strong sulphuric acid, effects the replacement of a second atom of hydrogen by $NO^2$, forming dinitrobenzole ($C^6H^4(NO^2)^2$), a crystalline solid.

Nitrobenzole is decomposed by sulphuretted hydrogen in presence of alcohol and ammonia, and by many other

reducing agents. Its oxygen is removed and replaced by two atoms of hydrogen, forming aniline ($C^6H^7N$).

Phenilic alcohol is accompanied in coal-tar creosote by a compound of analogous properties and higher boiling-point. This compound has been found to possess a composition corresponding to the formula $C^7H^8O$. It is homologous with phenilic alcohol, and is called cresylic alcohol.

Benzole, as first prepared from coal-tar before crystallization, is accompanied by the hydrocarbon toluol ($C^7H^8$). Nitric acid forms nitrotoluol ($C^7H^7NO^2$); and this body, the action of reducing agents, yields a base called toluidin ($C^7H^9N$), homologous with aniline.

**278. Aniline** ($C^6H^7N$ = 2 vols.; boiling-point, 182°; sp. gr. 1.028) is a constituent of coal-tar. It is, however, always prepared from benzole. Nitrobenzole is first prepared by the action of nitric acid on benzole, and is reduced by the action of a mixture of metallic iron and acetic acid. A very small quantity of acetic acid is employed compared to the iron, and the mass is constantly stirred while the action is going on between these materials and the nitrobenzole. Considerable heat is evolved in the process, and aniline distils out of the mixture together with its acetate. The acetate is decomposed by an alkali, and the mixture purified by distillation.

The benzole used for the manufacture of aniline usually contains toluol, and the product is accordingly accompanied by toluidin. It has been proved that the presence of toluidin is essential to the formation of the aniline red.

Aniline is a colourless liquid of very peculiar odour. It is scarcely soluble in water, and does not change the colour of red litmus-paper. Its vapour, however, forms white fumes with a rod moistened by hydrochloric acid. It is gradually coloured by contact with air, and ultimately transformed

into a brown resin. It decomposes ferrous and ferric salts, and many other salts of feeble bases.

It combines with acids in a similar manner to ammonia, forming salts which contain the elements of aniline in addition to those of the hydrogen compound. Thus—

$$C^6H^7N + HCl = C^6H^8NCl;$$
$$(C^6H^7N)^2 + H^2SO^4 = (C^6H^8N)^2SO^4.$$

Nearly all of its salts are soluble in water. They impart a yellow colour to fir-wood or to elder-pith. The compounds and derivatives of aniline have been chiefly investigated by Hofmann, and his researches have been fruitful of many important results.

**279.** Aniline is proved to be an ammonia in which one atom of hydrogen is replaced by phenyl, and in systematic nomenclature it is accordingly termed phenylamine, according to the formula $C^6H^5HHN$. Like ethylamine it is found to have two atoms of typical hydrogen in its molecule, as these two only can be replaced by ethyle or methyle, &c., forming ammonias, such as phenyl ethylia ($C^6H^5C^2H^5HN$), phenyl diethylia ($C^6H^5(C^2H^5)^2N$), phenyl eth-methylia ($C^6H^5C^2H^5CH^3N$), &c.

Its hydrochlorate yields by double decomposition with silver-nitrite an aniline nitrite, which immediately breaks up into phenilic hydrate, nitrogen, and water—

$$C^6H^8NNO^2 = C^6H^6O + H^2O + N^2.$$

Compounds in the type of ammonium chloride have also been obtained from aniline by the process which was described above as applying to triethia, &c. Thus diethphenilia combines with ethylic iodide, forming triethphenilium iodide—

$$C^6H^5(C^2H^5)^2N + C^2H^5I = C^6H^5(C^2H^5)^3NI.$$

Chlorine reacts violently on aniline, forming products of substitution. Three of these have been obtained by various processes—viz. chloraniline ($C^6H^6ClN$), a weaker base than aniline itself; dichloraniline ($C^6H^5Cl^2N$), a body endowed

with the feeblest basic properties; and trichloraniline, which is incapable of combining with acids. There are similar products containing bromine.

Aniline and its homologue toluidin have become important articles of manufacture for the preparation of the magnificent and varied dyes derived from them. Aniline had long been known to yield a blue colour when acted on by a hypochlorite, but the isolation of the gorgeous compounds which constitute the aniline dyes has certainly been one of the most remarkable applications of science to industrial art.

**280.** Among monatomic alcohols a remarkable body obtained by the decomposition of the essential oil of bitter almonds deserves mention. This oil is classed among aldehydes, for it absorbs oxygen from the air and yields benzoic acid—

$$C^7H^6O + O = C^7H^6O^2;$$

and it combines with hydrosodic sulphite as other aldehydes do.

Cannizzaro discovered that pure oil of bitter almonds is decomposed by alcoholic potash, forming potassic benzoate and benzoic alcohol—

$$(C^7H^6O)^2 + HKO = C^7H^5KO^2 + C^7H^8O.$$

This alcohol contains the radical $C^7H^7$ in the place of one atom of hydrogen of water, according to the formula $\begin{matrix}C^7H^7\\H\end{matrix}O$, and various products containing the radical $C^7H^7$ have been obtained from it by processes similar to those employed for preparing the corresponding derivatives from vinic alcohol. This benzoic alcohol has the same composition as cresylic alcohol. Its properties are, however, very different from those of the creosote.

A higher term of the same series has been obtained from cuminic aldehyde, the essential oil of cummin-seed. Cuminic aldehyde has a composition represented by the formula

$C^{10}H^{12}O$. Alcoholic potash decomposes it into potassic cuminate ($C^{10}H^{11}KO^2$) and cuminic alcohol ($C^{10}H^{14}O$).

A still higher term of this remarkable series of alcohols has been discovered by Messrs. De la Rue and Hugo Müller. It is a crystalline solid, melting at 90°, and having the composition $C^{18}H^{30}O$. It is called sycocerillic alcohol.

**281. Aldehydes** are a class of bodies analogous in their properties to common vinic aldehyde ($C^2H^4O$). They are a little superior to alcohols in their power of combining with bases; thus common aldehyde when dissolved in ether absorbs ammonia, and forms a crystalline compound possessing the composition $C^2H^3NH^4O$. Aldehydes absorb oxygen very freely, forming acids such as acetic acid ($C^2H^4O^2$), formed by the absorption of an atom of oxygen by vinic aldehyde. Another important property is that of combining with hydrosodic sulphite, forming compounds which are soluble in water, but insoluble or nearly so in a saturated aqueous solution of the double sulphite.

Vinic aldehyde ($C^2H^4O = 2$ vols.; boiling-point, 21°; sp. gr. 0.8) is usually prepared by the action of a mixture of sulphuric acid and red chromate on alcohol. The impure distillate is rectified at a gentle heat over calcic chloride, and what comes over is mixed with dry ether and precipitated as the ammonia compound by passing ammonia gas into the solution. This ammonia compound is easily decomposed by dilute sulphuric acid. Aldehyde is also formed by the destructive distillation of lactic acid—

$$C^3H^6O^3 = C^2H^4O + H^2O + CO.$$

It is a very volatile liquid which mixes in all proportions with water, and its solution reduces metallic silver in the form of a bright mirror from a solution of the nitrate, neutralized by ammonia. Caustic potash decomposes aldehyde, forming a brown resinous substance, whilst potassic acetate and formiate are formed. The compound formed

by combination of aldehyde with hydrosodic sulphite has the composition $C^2H^3NaSO^3$.

Vinic aldehyde is remarkable for the variety of isomeric bodies formed from it under various conditions. Four of these have been described; two of them being liquids very different from aldehydes in their properties, and two of them being solids.

An aqueous solution of aldehyde is decomposed by sulphuretted hydrogen, forming the compound $C^2H^4S$.

Chlorine gas passed to saturation into alcohol, forms amongst other products a body called chloral. **Chloral** is chlorinated aldehyde, having the composition $C^2HCl^3O$. It is oxidized by nitric acid, yielding chloracetic acid ($C^2HCl^3O^2$).

When caseine is distilled with a mixture of dilute sulphuric acid and manganic peroxide an acid liquid is collected, containing, amongst other products, vinic aldehyde ($C^2H^4O$), propionic aldehyde ($C^3H^6O$), butylic aldehyde ($C^4H^8O$), and benzoic aldehyde ($C^7H^6O$). Several aldehydes have been made by dry distillation of a mixture of a formiate with a salt. Thus a mixture of an acetate and formiate yields vinic aldehyde—

$$C^2H^3KO^2 + CHKO^2 = C^2H^4O + K^2CO^3.$$

In like manner benzoic aldehyde (oil of bitter almonds) has been obtained by distillation of a benzoate with a formiate—

$$C^7H^5KO^2 + CHKO^2 = C^7H^6O + K^2CO^3.$$

Chlorine gas replaces hydrogen in aldehyde, forming acetylic chloride ($C^2H^3OCl$), but this chloride combines with a molecule of the aldehyde.

**282.** The essential oil of **Cinnamon** consists of a mixture of a hydrocarbon with an aldehyde. Hydrosodic sulphite separates the aldehyde, and in the pure state it has the fragrant odour of the cinnamon and the composition

$C^9H^8O$. By absorbing oxygen it forms cinnamic acid ($C^9H^8O^2$).

Another aldehyde has long been known by the name of oil of ants, from the circumstance of its being formed in the preparation of formic acid, by the action of dilute sulphuric acid and manganic binoxide upon starch, &c. The substance is usually called **Furfurol**, and is best prepared from bran, by boiling with sulphuric acid diluted with double its weight of water, or with a concentrated solution of zinc chloride.

Furfurol has the composition $C^5H^4O^2$; boiling-point, 162°. It dissolves readily in water, and gradually absorbs oxygen from the air, becoming resinous. Furfurol reduces silver oxide, forming pyromucic acid ($C^5H^4O^3$).

**Acrolein** is the name given to a volatile body of most pungent odour, formed by the dry distillation of glycerine or its compounds. Acrolein has the composition $C^3H^4O$. It is analogous to aldehydes in its properties. Acrylic acid ($C^3H^4O^2$) is formed by its oxidation.

Aldehydes in general react upon ammonia, their oxygen uniting with the hydrogen of the alkali, and two atoms of nitrogen taking the place of three atoms of oxygen. Thus bitter almond oil forms a compound called **Hydrobenzamide**—

$$C^{21}H^{18}N^2 = (C^7H^6O)^3 + (NH^3)^2 - (H^2O^3).$$

Aqueous hydrochloric acid easily decomposes hydrobenzamide, water being taken up, and benzoic aldehyde and ammonia reproduced. By ebullition with caustic potash hydrobenzamide is transformed into an isomeric body of considerable stability. This body is called amarine. It is not decomposed like hydrobenzamide by hydrochloric acid, but unites with it, forming the salt $C^{21}H^{18}N^2HCl$.

Furfurol also unites with ammonia, forming a solid amide called furfuramide, containing—

$$(C^5H^4O^2)^3 + (NH^3)^2 = C^{15}H^{12}O^3N^2 + (H^2O)^3.$$

Furfuramide resembles hydrobenzamide in the facility with which it is decomposed by aqueous acids into furfurol and ammonia. When boiled in an excess of caustic potash furfuramide is transformed into its isomeric furfurine ($C^{15}H^{12}O^3N$), a base of considerable stability.

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# CHAPTER XLV.

**283. Acetone** is a compound resembling aldehyde in several of its properties, and a numerous class of bodies of the same family as acetone have similar resemblances with aldehydes. This class of bodies like acetone is called the ketones.

Acetone ($C^3H^6O$ = 2 vols.; boiling-point, 55°; sp. gr. 0.8) is a constituent of wood-spirits. It is easily obtained in a state of purity by distilling sodic acetate. Two molecules of the salt react on one another, forming sodic carbonate and acetone—

$$(C^2H^3NaO^2)^2 = Na^2CO^3 + C^3H^6O.$$

Acetone is a neutral liquid of an agreeable ethereal odour. It mixes in all proportions with water, but is precipitated from this solution in the form of a light oil by saturating the water with potash. Alcohol is not precipitated from its aqueous solution by potash. Acetone combines like an aldehyde with hydrosodic sulphite, and the compound has properties analogous to those of the corresponding aldehyde compound.

Potassic hydrate decomposes the vapour of acetone, forming potassic acetate and marsh gas—

$$C^2H^3OCH^3 + KOH = C^2H^3KO^2 + CH^3H.$$

This reaction assimilates acetone to aldehyde, which under

similar circumstances forms potassic acetate and free hydrogen—

$$C^2H^3OH + KOH = C^2H^3KO^2 + HH.$$

The formation of acetone from two molecules of monatomic acetate favours the view that its molecule is formed by the union of an atom of methyle with an atom of the radical $C^2H^3O$, called acetyl. For if we arrange the elements of one molecule of potassic acetate in two groups thus—$(C^2H^3O)(KO)$, and the elements of another molecule in two other groups thus—$(CH^3)(CKO^2)$, it is evident that a double decomposition between the two will give us the compounds actually found to be formed—

$$(C^2H^3O)(KO) + (CH^3)(CKO^2) = (C^2H^3O)(CH^3) + (KO)(CKO^2).$$

Under the influence of most reagents acetone does not, however, break up in accordance with this view of its constitution. Thus hydrochloric acid or phosphoric chloride gives rise to the formation of a chloride called mesitylic chloride ($C^3H^5Cl$). Sulphuric acid forms amongst other products the hydrocarbon mesitylene ($C^9H^{12}$). Another product is the so-called mesitylic oxide ($C^6H^{10}O$), which has been considered as the ether of acetone.

A crystallizable compound called **Benzophenone** is obtained by the distillation of calcic benzoate—

$$Ca(C^7H^5O^2)^2 = CaCO^3 + C^7H^5OC^6H^5.$$

Potassic hydrate decomposes benzophenone, forming potassic benzoate and phenylic hydride (benzole)—

$$C^7H^5OC^6H^5 + HKO = C^7H^5KO^2 + C^6H^5H.$$

When a mixture of two salts homologous with the acetates is distilled, a ketone is built up partly from the elements of one molecule, partly from those of the other. Thus a mixture of an acetate and a valerate distilled together gives rise to the formation of the ketone—

$$C^6H^{12}O = C^2H^3KO^2 + C^5H^9KO^2 - CK^2O^3.$$

The formation of aldehydes by the distillation of a formiate with another salt is a particular class of cases belonging to this general reaction.

**284.** The series of acids homologous with acetic acid is usually named after that most important term the 'acetic series.'

The first term of the series (formic acid) has been described among inorganic compounds, to which it may fairly be considered as belonging since Berthelot's synthetical formation of potassic formiate from potassic hydrate and carbonic oxide.

**Acetic Acid** ($C^2H^4O^2$ = 2 vols.; boiling-point, 120°) is largely prepared in the impure state for domestic use, and sold by the name of vinegar. The process of its formation is an oxidation of alcohol in presence of water, and under the influence of an organism commonly called vinegar plant (*mycoderma aceti*). A wort made usually from malt is subjected to alcoholic fermentation, and the 'wash,' or weak alcoholic liquid thus obtained, is allowed to settle, so that the yeast may separate from it as completely as possible. Large vats are filled to near the top with pieces of flat wicker-work like short pieces of board. The new vat-full of new wicker is watered for several days with wash partially converted into vinegar in an old vat. This wash contains abundant germs of the mycoderma, and after a few days the surface of the wicker in the new vat is found covered with a growth of the plant, which goes on increasing during the subsequent use of the vat until it nearly fills up the spaces between the pieces of wicker, through which the wash must trickle. The vat and its contents are then cleared of the greater part of the organic growth, and set to work again. When a vat is in full work a stream of wash, either fresh or partially acetified, is being distributed over the top of the wicker, and is trickling down over it and in

contact with the mycoderma. At the same time a current of air enters by holes at the bottom of the vat, and passes upwards to outlets at the top of the vat, where it escapes after giving up a part of its oxygen to the alcohol. Each molecule of alcohol absorbs two atoms of oxygen, forming water and acetic acid—

$$C^2H^6O + O^2 = H^2O + C^2H^4O^2.$$

The process is accompanied by the evolution of heat, and a vat with its contents, when in full work, is found to be heated to about 35°. This heat, of course, causes an upward draught of the air in the vat, which establishes the circulation necessary for a continuance of the process of oxidation.

Some of the brown vinegar obtained in this way is purified by distillation, and then sold in the form of colourless and nearly pure acetic acid. The brown undistilled acetic acid no doubt contains the glycerine and succinic acid which were formed by the vinous fermentation of the wort.

Acetic acid is also largely prepared by the destructive distillation of wood, and is often called pyroligneous acid when obtained from that source. The watery part of the crude distillate from wood is separated from the tar, and neutralized by lime. When this mixture is distilled, impure wood-naphtha goes over with water, and crude calcic acetate is left behind. The tarry colourless matters which at first accompany the acid are easily rendered insoluble by heating sodic acetate. On dissolving the acetate in water a nearly colourless solution is obtained. The acid is obtained by distillation of its sodium-salt with sulphuric acid, or sometimes of its calcium-salt with hydrochloric acid.

**285.** The pure hydric acetate is often called glacial acetic acid, from its property of crystallizing at low temperatures. It is most easily obtained on a small scale by dividing a given quantity of the dilute acid into two equal parts, neutralizing one of these by potash, then mixing it with the

other, and evaporating the mixture. When nearly dry the mixture should be poured into a retort. By raising the temperature gradually the water can be completely expelled, leaving a substance of the composition $C^2H^3KO^2C^2H^4O^2$—a compound in which potassic acetate is united with hydric acetate in a loose manner similar to that in which it unites with water of crystallization. At 200° this compound is decomposed, giving off the pure hydrogen salt, or glacial acetic acid.

Acetic acid forms with one molecule of water a compound $C^2H^3KO^2H^2O$, of which the density is 1.073. Solutions containing a greater proportion of acid have a smaller specific gravity, that of the glacial acid being 1.063. More dilute solutions have also a lower density.

The metallic acetates are for the most part very soluble in water. Silver acetate ($AgC^2H^3O^2$) is one of the least soluble. Ferric and aluminic acetates are decomposed by ebullition of their aqueous solution, acetic acid being carried away by the steam and an oxy-salt being precipitated. A similar decomposition takes place more slowly when a solution of one of these salts is spread over the surface of a cotton fabric, and hung up in a moist and warm atmosphere. This process is called 'aging' by the cotton-printers, and it effects a deposition of ferric oxyacetate or aluminic oxyacetate on the fibres of the cloth, while acetic acid evaporates. This deposit of the ferric or aluminic compound is called a 'mordant.'

**286. Plumbic Acetate** is one of the commonest salts of the acid. It is usually known by the name 'sugar of lead.' Its crystals contain three molecules of water of crystallization; $Pb(C^2H^3O^2)^2(H^2O)^3$.

An aqueous solution of this salt dissolves plumbic oxide readily, and acquires thereby an alkaline reaction and the property of becoming turbid by contact with carbonic acid.

Plumbic hydroacetate $\left(Pb\begin{matrix}C^2H^3O^2\\H\ O\end{matrix}\right)$ appears to be formed by the action of lead oxide on the acetate; but when more oxide is employed, triplumbic dioxyacetate ($Pb^3O^2(C^2H^3O^2)^2$) is formed. A solution of this salt is used in pharmacy by the name of 'goulard water.'

Compounds of copper with acetic acid are formed by exposure of metallic copper, together with acetic acid, to the air. They are popularly called 'verdigris.' There is not only a normal cupric acetate ($Cu(C^2H^3O^2)^2$), but also a cupric hydroacetate ($Cu\,H\,O\,C^2H^3O^2$).

The name 'emerald green' is given to a beautiful cupric acetoarsenite of the composition $Cu\begin{matrix}C^2H^3O^2\\As\,O^2\end{matrix}$.

Acetic acid combines with the monatomic alcohol radicals, forming so-called **Compound Ethers**. These ethers are formed, together with water, by heating the acid with the alcohol, but the presence of sulphuric or hydrochloric acid is found to accelerate greatly the process of combination. When thus used, the mineral acid is termed an etherifying agent. The action of sulphuric acid is, no doubt, of the same kind as in the formation of ether and water from alcohol; viz. first, the formation of sulphovinic acid and water, then by the action of sulphovinic acid on acetic acid the formation of acetic ether and the reproduction of sulphuric acid—

$$\begin{matrix}C^2H^5\\H\end{matrix}SO^4 + \begin{matrix}H\\C^2H^3O\end{matrix}O = \begin{matrix}C^2H^5\\C^2H^3O\end{matrix}O + \begin{matrix}H\\H\end{matrix}SO^4;$$

like $\begin{matrix}H\\H\end{matrix}SO^4 + \begin{matrix}C^2H^5\\H\end{matrix}O = \begin{matrix}C^2H^5\\H\end{matrix}SO^4 + \begin{matrix}H\\H\end{matrix}O.$

**Acetic Ether** has an agreeable odour, by which its presence can be detected when it is not mixed with other odorous bodies. Its boiling-point is 74°, whilst that of methylic acetate is 58°, butylic acetate 114°, and amylic acetate

boils at 125°. Mixtures of these ethers, and of others containing homologues of acetic acid, are no doubt present in various small proportions in wines, and contribute to their characteristic 'bouquet.'

Acetic ether is decomposed by ammonia, forming alcohol and acetamide—

$$\begin{matrix} C^2H^5 \\ C^2H^3O \end{matrix} O + NH^3 = \begin{matrix} C^2H^5 \\ H \end{matrix} O + NH^2(C^2H^3O).$$

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# CHAPTER XLVI.

**287.** Acetic acid is decomposed by chlorine under the influence of sunshine. Three products of substitution have been prepared—viz. chloracetic acid, $\begin{matrix} C^2H^2ClO \\ H \end{matrix} O$, dichloracetic acid, $\begin{matrix} O^2HCl^2O \\ H \end{matrix} O$, and trichloracetic acid, $\begin{matrix} C^2Cl^3O \\ H \end{matrix} O$. They are monobasic, like acetic acid itself, though no doubt stronger.

**Thiacetic Acid** is a compound formed by the action of phosphoric sulphide on acetic acid—

$$\begin{matrix} C^2H^3O \\ H \end{matrix} O + P^2S^5 = \begin{matrix} C^2H^3O \\ H \end{matrix} S + P^2OS^4.$$

It boils at 93°.

Sulphacetic acid is formed by the action of anhydrous sulphuric acid on acetic acid. Its formation is analogous to that of sulphovinic acid, for it contains the elements of a molecule of hydrated acetic acid in addition to those of a molecule of anhydrous acid—

$$\begin{matrix} C^2H^3O \\ H \end{matrix} O + SO^3 = \begin{matrix} C^2H^3O \\ H \end{matrix} SO^4.$$

It forms a potassium salt of the empirical formula $C^2H^2K^2SO^5$, and a barium salt ($C^2H^2BaSO^5$), which is slightly soluble in water.

**288. Propionic Acid** ($C^3H^6O^2$) has obtained its name from the circumstance of its being the first acid of the series which can be precipitated, like an oily compound, from its aqueous solution by calcic chloride or glacial phosphoric acid. It is best obtained by the action of potash on vinic cyanide—

$$C^2H^5CN + H^3KO^2 = C^3H^5KO^2 + NH^3.$$

Butyric acid was first obtained by Chevreuil among the constituents of butter. It is most advantageously prepared by leaving calcic lactate with water and old cheese at a temperature of 35°. Hydrogen and carbonic acid are given off during the process of fermentation which takes place, and the lactic acid is entirely destroyed, butyric acid being formed in its place. Acetic and valerianic acids are frequently formed in smaller quantity at the same time.

Butyric acid boils at 159°. Its density is 0.9886 at 0°C. It dissolves in water in all proportions. Its salts are in general soluble in water. It forms ethers, each of them boiling at a higher temperature than the corresponding acetate. They are also less soluble in water than the acetic ethers.

**289. Valerianic Acid** ($C^5H^{10}O^2$; boiling-point, 175°–180°; sp. gr. 0.937). This acid has obtained its name from the valerian root from which it was extracted. It is present in rancid cheese and in many other decomposed organic mixtures. It is best obtained by the action of amylic alcohol on a solution of potassic dichromate acidulated by sulphuric acid. On distilling the mixture an acid distillate is obtained containing valerianic aldehyde and valerianic acid, which can easily be separated by potash. Valerianic acid requires about thirty volumes of water for its solution; and when added in

greater quantity the acid floats as an oily stratum upon the aqueous solution. The oily stratum is a compound of valerianic acid with a molecule of water ($C^5H^{10}O^2H^2O$), having a density greater than that of the acid itself, viz. 0.95.

Valerianic acid has an exceedingly persistent and unpleasant odour.

**Caproic Acid** ($C^6H^{12}O^2$) was obtained from the liquid part of cow's butter. Butter was melted, and pressed after cooling. The solid crystalline residue, consisting of margaric and other solid acids combined with glycerine, was put aside, and the liquid portion was dissolved in potash by the aid of heat, or, as it is called, saponified. The aqueous solution of the soap was precipitated by salt, and the soap thus obtained was decomposed by dilute sulphuric acid, and distilled. In this manner an acid distillate was obtained, consisting of water holding several acids in solution, and having oily drops of acid floating upon it. The mixture was neutralized by baryta water, and the barytic salts thus obtained were separated by crystallization. In this manner salts of butylic, caproic, caprilic ($C^8H^{16}O^2$), and capric acid ($C^{10}H^{20}O^2$) were obtained, the butyrate being the most soluble in water, and the solubility of the others diminishing with the increase of their atomic weight.

Caproic acid boils at about 198°. It is most easily obtained by the decomposition of amylic cyanide. The next acid of the series, viz. œnanthylic ($C^7H^{14}O^2$), is obtained by distilling castor oil with nitric acid. The œnanthylic acid comes over with the vapour of water and is collected in the receiver.

**Caprilic Acid** ($C^8H^{16}O^2$; boiling-point, 236°–240°) is most conveniently prepared from cocoa-nut oil.

**Pelargonic Acid** ($C^9H^{18}O^2$; boiling-point, 260°) was first prepared from geranium leaves. Gerhardt recommends oil of rue for its preparation. This oil is distilled with dilute

nitric acid, and the distillate neutralized by baryta and crystallized. Ethylic pelargonate appears to be the chief constituent of the so-called oil of wine—a fragrant oil which is used for flavouring purposes. Capric or rutic acid ($C^{10}H^{20}O^2$) has been found in the fousel oil of whiskey. Its barytic salt ($Ba(C^{10}H^{19}O^2)^2$) is purified by repeated crystallizations and then decomposed by sodic carbonate. The addition of dilute sulphuric acid to the sodic salt precipitates the acid in the solid form.

Lauric acid ($C^{12}H^{24}O^2$) melts at 42° or 43°.

Cocinic acid ($C^{13}H^{26}O^2$) is said to have been obtained by saponifying cocoa-nut oil and decomposing the soap by hydrochloric acid. In this manner an oily mixture of acids is obtained, from which cocinic acid crystallizes out. The liquid acids are pressed out from the mass by a hydraulic press. The impure cocinic acid thus obtained is dissolved in hot alcohol, and purified by repeated crystallizations. It is ultimately obtained with a melting-point of 42° to 43°.

There seems some reason to believe that the acid thus obtained was a mixture.

Myristic acid ($C^{14}H^{28}O^2$) melts at 49°.

The next term of the series is called benic acid—

$$C^{15}H^{30}O^2.$$

**290. Palmitic** or **Cetylic Acid** ($C^{16}H^{32}O^2$) melts at 62°. It is obtained from palm oil in the same way as cocinic acid from cocoa-nut oil, or from spermaceti after decomposition by alcoholic potash. Palmitic acid is frequently used for the manufacture of so-called composition candles. For this purpose the acids of palm oil can be liberated by the action of sulphuric acid, and purified by distillation in superheated steam. It has, however, been found that the palm oil itself is decomposed by the action of superheated steam into free acids and glycerine. These products are condensed from the steam, and the liquid

acids removed by the action of a powerful hydraulic press from the palmitic and other solid acids. Water heated to a high temperature in a Papin's digester likewise decomposes palm oil and most other fats.

**Margaric Acid** ($C^{17}H^{34}O^2$) is stated to occur in combination with glycerine in many common oils and fats, such as olive oil, butter, goose fat, human fat, &c.

Its melting-point is given at 60°, and according to analogy it might be higher than 62°, the melting-point of palmitic acid, instead of lower. There seems some reason to suspect that what has passed for margaric acid is a mixture of palmitic acid with stearic acid. The former of these melts at 62° and the latter at 69° or 70°, but a mixture of the two has been found to melt at as low a temperature as 54°, and mixtures containing greater proportions of stearic acid melt at higher temperatures.

An acid possessing the composition of margaric acid has been made by the action of potassic hydrate on cetylic cyanide—

$$C^{16}H^{33}CN + H^3KO^2 = C^{17}H^{33}KO^2 + NH^3.$$

This artificial margaric acid melts below 60°.

**291. Stearic Acid** ($C^{18}H^{36}O^2$) is contained in beef and mutton suet, together with other acids, combined with glycerine. To obtain the acid in a state of purity from a mixture in which it is accompanied by homologues of lower atomic weight, Heintz's process of partial precipitation should be resorted to. This process consists in dissolving in alcohol the soap containing the stearic acid, and adding to the solution at the temperature of ebullition an alcoholic solution of barytic or magnesic acetate in very small quantity. Stearic acid is under these circumstances precipitated before palmitic acid or other acids containing less carbon in their molecule, and if the quantity of acetate employed be small enough, no palmitic or lower acid goes down with the stearate.

Stearic acid crystallizes in shining needles. It decomposes alkaline carbonates with effervescence, forming a so-called soap. Potassic and sodic stearates are very soluble in water, and are alkaline to test-paper. Water saturated with sodic chloride does not dissolve soaps, and the addition of salt precipitates soap from its solution. Solutions of alkaline stearates are decomposed on dilution into alkali, and stearic acid, which is precipitated together with an equivalent of the soap. The compounds with the alkaline earths and heavy metallic oxides are insoluble in water. The potash and soda salts dissolve in alcohol, but not in ether.

Stearic acid is insoluble in water, but dissolves in alcohol, and the solution has an acid reaction to test-paper.

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# CHAPTER XLVII.

**292.** An exceedingly common accompaniment of the acids of this series is **Oleic Acid.** The glycerine compound of oleic acid, called oleine, is liquid and uncrystallizable, whereas stearic and palmitic acid, &c. form with glycerine compounds called stearine and palmitine, and which are solid at the ordinary atmospheric temperature, and which crystallize out from their solution in oleine on cooling. Thus olive oil in cold weather deposits crystals of palmitine, &c., while oleine remains fluid and can be pressed out from the crystals. Alkaline oleates are not decomposed by dilution with water, as stearates, &c. are; and by neutralizing the alkali liberated by the dilution of a concentrated solution

of a stearate, and then diluting again, some more stearate is decomposed, and it is stated that the whole of the stearic acid can be separated from a mixture with oleic acid, by a frequent repetition of this process. Oleine is more soluble in ether than stearine or palmitine, and can in great part be separated from the solid fats by washing with ether.

Plumbic oleate is readily soluble in ether, whereas plumbic palmitate or stearate, &c. are nearly insoluble.

Oleic acid is represented by the formula $C^{18} H^{34} O^2$.

A mixture of lead salts of the fatty acids is used by the name of plaster. Olive oil is frequently used for the preparation of plaster. Litharge in presence of water gradually decomposes it at 100°, liberating the glycerine.

Many oils—such as those expressed from the seeds of lint, poppy, walnut, hemp, ricinus, or castor-oil plant—possess the property of becoming thick, and ultimately hard and resinous, by exposure to the air. This process takes place still more rapidly if the oil has been heated with litharge. These so-called 'drying' oils are used by painters to fix their colours. Lint-seed oil and poppy oil appear to contain an acid of the composition $C^{16} H^{28} O^2$, to the oxidation of which this 'drying' process is due.

The acid containing $C^{20} H^{40} O^2$ is called arachinic acid, and the one containing $C^{22} H^{44} O^2$ is behenic acid.

Hyenic acid ($C^{25} H^{50} O^2$; melting-point, 77° to 78°) has been found in the fat of the hyæna.

**293. Cerotic Acid** ($C^{27} H^{54} O^2$) is contained in beeswax, and can be dissolved out from it by alcohol. Its melting-point is given at 78°.

Melissic acid ($C^{30} H^{60} O^2$) has been obtained from melissic alcohol by fusion with potassic hydrate. It melts at 88° to 89°.

All the acids of this series, frequently called the adipic series, are oxidized by boiling nitric acid. Two classes of

products are formed in the process — viz. lower acids of the same series, such as caproic, œnanthic, caprilic, &c., which pass over into the receiver, and acids homologous with oxalic acid, which remain in the retort.

**294.** Phosphoric chloride decomposes acetic acid exactly in the same manner as it decomposes alcohol, forming chlorophosphoric acid, hydrochloric acid, and the chloride of the radical acetyl—

$$\begin{matrix} C^2H^3O \\ H \end{matrix} O + P Cl^5 = P O Cl^3 + H Cl + Cl^2H^3O Cl.$$

The action is exceedingly energetic, and the acetic chloride can be distilled over at a gentle heat, leaving the greater part of the chlorophosphoric acid behind. Acetic chloride is a liquid heavier than water, and boiling at ·55°. It has a very pungent odour; and in contact with moisture it is rapidly decomposed, forming hydrochloric acid and acetic acid—

$$C^2H^3O Cl + \begin{matrix} H \\ H \end{matrix} O = H Cl + \begin{matrix} C^2H^3O \\ H \end{matrix} O.$$

In this decomposition acetic acid is formed by replacing one atom of hydrogen in water by an atom of acetyl. Acetic chloride reacts very violently on ammonia, removing one atom of hydrogen from a molecule of the volatile alkali and replacing it by an atom of acetyl—

$$C^2H^3O Cl + (N H^3)^2 = N H^2 C^2 H^3 O + N H^4 Cl.$$

This ammonia, containing acetyl in the place of one atom of hydrogen, is called **Acetamide**. It is obtained by heating ammonia acetate, so as to remove half the oxygen of that salt in combination with hydrogen—

$$\begin{matrix} C^2H^3O \\ N H^2 H^2 \end{matrix} O = \begin{matrix} C^2H^3O \\ N H^2 \end{matrix} + H^2O.$$

In contact with alcohol, acetic chloride forms hydrochloric acid and acetic ether—

$$\begin{matrix} C^2H^5 \\ H \end{matrix} O + C^2H^3O Cl = \begin{matrix} C^2H^5 \\ C^2H^3O \end{matrix} O + H Cl.$$

**295.** With potassic acetate it forms anhydrous acetic acid by replacing the potassium in the salt by acetyle—

$$C^2H^3OCl + \begin{matrix}C^2H^3O\\K\end{matrix}O = \begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}O + KCl.$$

According to this reaction anhydrous acetic acid is a molecule of water in which the two atoms of hydrogen are replaced by two atoms of acetyl; the hydrate being a molecule of water in which one atom of hydrogen is replaced by one of acetyl.

Anhydrous acetic acid boils at 138°. It sinks in water, and does not appear to dissolve in it as such. It, however, gradually decomposes the water, forming two molecules of hydrated acid—

$$\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}O + \begin{matrix}H\\H\end{matrix}O = \begin{matrix}C^2H^3O\\H\end{matrix}O + \begin{matrix}H\\C^2H^3O\end{matrix}O.$$

Its reactions are in general similar to those of acetic chloride, the group $C^2H^3O^2$ acting like chlorine. Thus with ammonia it forms ammonia acetate and acetamide—

$$\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}O + (NH^3)^2 = NH^2C^2H^3O + \begin{matrix}C^2H^3O\\NH^4\end{matrix}O.$$

Phosphoric chloride decomposes anhydrous acetic acid, forming phosphoric oxychloride and acetic chloride—

$$\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}O + PCl^5 = (C^2H^3OCl)^2 + POCl^3.$$

Formic acid does not yield similar products to acetic acid. When acted upon by phosphoric chloride the formic chloride breaks up into carbonic oxide and hydrochloric acid—

$$\begin{matrix}CHO\\H\end{matrix}O + PCl^5 = POCl^3 + (HCl)^2 + CO.$$

Anhydrous formic acid has not as yet been obtained. Propionic, butyric, valerianic, and the higher acids of the adipic series, all yield chlorides homologous with acetic chloride ($C^3H^5OCl$, $C^4H^7OCl$, $C^5H^9OCl$, &c.), and these chlorides, in their turn, react like acetic chloride on the potassium salts of their acids, forming anhydrous propionic

acid $\left(\begin{matrix}C^3H^5O\\C^3H^5O\end{matrix}O\right)$, anhydrous butyric acid $\left(\begin{matrix}C^4H^7O\\C^4H^7O\end{matrix}O\right)$, anhydrous valerianic acid $\left(\begin{matrix}C^5H^9O\\C^5H^9O\end{matrix}O\right)$, &c.

**296.** Several terms of a series of monatomic acids have been discovered containing in each molecule two atoms of hydrogen less than the corresponding acids of this series. The first of these, called **Acrylic Acid** ($C^3H^4O^2$), is formed from acrolein by absorption of oxygen.

Crotonic acid ($C^4H^6O^2$) has been found in the croton-seed oil.

Angelic acid ($C^5H^8O^2$) is present in angelica root.

The other acids considered to belong to this series are :—

| | |
|---|---|
| Pyroterebic acid ($C^6H^{10}O^2$). | Hypogeic acid ($C^{16}H^{30}O^2$). |
| Damaluric acid ($C^7H^{12}O^2$). | Oleic acid ($C^{18}H^{34}O^2$). |
| Campholic acid ($C^{10}H^{18}O^2$). | Brassic acid ($C^{22}H^{42}O^2$). |
| Moringic acid ($C^{15}H^{28}O^2$). | |

Oleic acid is the liquid constituent of a great many non-drying oils.

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# CHAPTER XLVIII.

**297.** Another series of monatomic acids homologous with benzoic acid is called the aromatic series.

**Benzoic Acid** ($C^7H^6O^2$) is the first and most important term of the series. It is contained in gum benzoin, and is best extracted by boiling the powdered gum resin with milk of lime, filtering off the solution of calcic benzoate thus obtained, and precipitating the acid from it by hydrochloric acid. Benzoic acid is present in large quantities in the putrid urine of horses and cows, and can be obtained

in the crystalline state by evaporating the decomposed urine. Fresh urine of these herbivorous animals contains no benzoic acid, but in its place hippuric acid ($C^9H^9NO^3$). Hippuric acid breaks up under the influence of ferments, or of hot hydrochloric acid. It takes up the elements of a molecule of water, forming benzoic acid and an amide called glycocoll—

$$C^9H^9NO^3 + H^2O = C^7H^6O^2 + C^2H^5NO^2.$$

The glycocoll decomposes further in the decomposing urine.

Benzoic acid is a solid compound of very crystalline structure. It melts easily, and can be sublimed with very slight decomposition. It is very slightly soluble in water, but sufficiently so to impart to it a decidedly acid reaction. Its salts with the alkalies and alkaline earths are readily soluble in water. They are of one class only, viz. normal salts, such as potassic benzoate ($KC^7H^5O^2$), calcic benzoate ($Ca(C^7H^5O^2)^2$), &c. With ferric oxide the acid forms a salt insoluble in water.

Barytic benzoate is not precipitated from its aqueous solution by alcohol in presence of ammonia chloride.

Potassic benzoate distilled with potassic formiate yields benzoic aldehyde, the essential oil of bitter almonds—

$$\begin{matrix} C^7H^5O \\ K \end{matrix} O + \begin{matrix} CHO \\ K \end{matrix} O = C^7H^5OH + CO^3K^2.$$

The oil is thus formed by the combination of hydrogen with the radical benzoile ($C^7H^5O$).

**298.** When potassic benzoate is distilled by itself, a perfectly similar reaction takes place between two molecules of the salt; one molecule furnishing phenyl, and the other furnishing benzoile—

$$\begin{matrix} C^7H^5O \\ K \end{matrix} O + \begin{matrix} C^6H^5CO \\ K \end{matrix} O = C^7H^5OC^6H^5 + CO^3K^2.$$

The analogy between benzoic hydride and benzoic phenylide is moreover not confined to the circumstances of their formation; for when they are heated with potassic hydrate

both compounds form potassic benzoate by replacing the hydrogen of the hydrate by benzoile, while in each case this expelled hydrogen takes the place of the benzoile, forming in one case a molecule of free hydrogen (hydric hydride), in the other case phenylic hydride—

$$C^7H^5OH + \frac{H}{K}O = \frac{C^7H^5O}{K}O + HH;$$

$$C^7H^5OC^6H^5 + \frac{H}{K}O = \frac{C^7H^5O}{K} + C^6H^5H.$$

Chlorine decomposes benzoic hydride, forming benzoic chloride and hydrochloric acid—

$$C^7H^5OH + ClCl = C^7H^5OCl + HCl.$$

Phosphoric chloride decomposes benzoic acid, forming this same benzoic chloride—

$$\frac{C^7H^5O}{H}O + PCl^5 = C^7H^5OCl + HCl + POCl^3.$$

**Benzoic Chloride** corresponds in its general reactions to acetic chloride, and other compounds of chlorous radicals with chlorine. It reacts on potassic benzoate, forming anhydrous benzoic acid—

$$C^7H^5OCl + \frac{C^7H^5O}{K}O = \frac{C^7H^5O}{C^7H^5O}O + KCl.$$

With potassic acetate it forms an anhydrous acid, containing acetyl and benzoile in one molecule—

$$C^7H^5OCl + \frac{C^2H^3O}{K}O = \frac{C^2H^3O}{C^7H^5O}O + KCl.$$

Benzoic ether is a fragrant oil somewhat heavier than water. It boils at 209°.

Toluilic acid ($C^8H^8O^2$) is obtained by the action of very dilute nitric acid on a hydrocarbon called eymene, or cymol. Its reactions and decompositions correspond to those of benzoic acid.

Cuminic acid ($C^{10}H^{12}O^2$) is obtained by the oxidation of its aldehyde, which occurs in the volatile oil of cumminseed.

**299.** The lower terms of the adipic series combine with ammonia in one proportion, similar to that in which other monobasic acids combine with it. Thus ammonia formiate and acetate have the formulæ—

$$NH^4CHO^2; \quad NH^4C^2H^3O^2.$$

When ammonia reacts on an ether of one of these acids alcohol is formed together with an amide. Thus acetic ether $\left(\begin{matrix}C^2H^5\\C^2H^3O\end{matrix}O\right)$ with ammonia forms acetamide ($C^2H^3ONH^2$) and alcohol.

**Acetamide** is also formed by the dry distillation of ammonia acetate. It is a crystalline solid, having very nearly neutral properties; for on the one hand it combines feebly with nitric or hydrochloric acid, on the other hand it is decomposed by potassium, with evolution of hydrogen and formation of a weak salt. Products formed like acetamide by the replacement of hydrogen in ammonia by a radical of chlorous properties are called amides. Acetamide is a primary amide. When two atoms of hydrogen are so replaced as in the diacetamide $(C^2H^3O)^2NH$, the compound is termed a secondary amide, and tertiary amides are single molecules of ammonia in which all the typical hydrogen is replaced by chlorous radicals.

There are also ammonias in which the typical hydrogen is replaced partly by basylous radicals such as the alcohol radicals, partly by chlorous radicals. Thus by the action of anhydrous acetic acid on cyanic ether may be prepared an ammonia containing two atoms of acetyle and one of ethyl—

$$N\begin{matrix}CO\\C^2H^5\end{matrix} + \begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}O = N\begin{matrix}(C^2H^3O)^2\\C^2H^5\end{matrix} + CO^2.$$

**300. Diatomic Alcohols** are compounds formed on the type of two molecules of water; one atom of a hydrocarbon replacing two atoms of hydrogen in them, one in one molecule of water, the other in the other molecule.

Ethylene ($C^2H^4$) is a hydrocarbon, of which one atom is capable of replacing two atoms of hydrogen, or of combining with two atoms of chlorine. A molecule of ethylenic bromide ($C^2H^4Br^2$) reacts on two molecules of argentic acetate, forming argentic bromide and ethylenic acetate—

$$C^2H^4Br^2 + \begin{matrix} C^2H^3O \\ Ag \\ Ag \\ C^2H^3O \end{matrix} O = (AgBr)^2 + \begin{matrix} C^2H^3O \\ C^2H^4 \\ C^2H^3O \end{matrix} O_2.$$

The reaction is parallel to that of zinc bromide ($ZnBr^2$) on argentic acetate, an atom of zinc forming the acetate $Zn(C^2H^3O^2)^2$, just as an atom of ethylene forms ethylenic acetate ($C^2H^4(C^2H^3O^2)^2$).

By the action of potash on this acetate the ethylenic hydrate is obtained $C^2H^4(HO)^2$, in the form of a liquid, soluble in water in all proportions, and having a sweet taste. It distils without decomposition at 197.5°.

This remarkable body was named **Glycol** by its discoverer, Wurtz. It reacts upon monobasic acids in two proportions.

Thus hydrochloric acid forms ethylenic hydrochloride, $C^2H^4\begin{matrix} Cl \\ HO \end{matrix}$, and by the action of phosphoric chloride on this body the normal chloride $C^2H^4Cl^2$ is obtained, just as the diatomic radical $SO^2$ of the sulphates forms not only the normal hydrate $SO^2(HO)^2$, but also by the action of phosphoric chloride the hydrochloride $SO^2\begin{matrix} Cl \\ HO \end{matrix}$, and the normal chloride $SO^2Cl^2$.

With acetic acid, glycol forms the normal ethylenic acetate $C^2H^4\begin{matrix} C^2H^3O^2 \\ C^2H^3O^2 \end{matrix}$, and also ethylenic hydroacetate—

$$C^2H^4\begin{matrix} HO \\ C^2H^3O^2 \end{matrix}.$$

Sodium decomposes glycol, with evolution of hydrogen, forming in the first instance the compound $\begin{matrix}C^2H^4\\Na\,H\end{matrix}O^2$.

By prolonged heating with sodium the second atom of hydrogen is with difficulty expelled, forming the compound $\begin{matrix}C^2H^4\\Na^2\end{matrix}O^2$.

**301. Ethylenic Oxide** ($C^2H^4O$) has not been obtained by processes similar to those by which ethylic oxide is obtained from alcohol. Zinc chloride decomposes glycol with the aid of heat, forming vinic aldehyde, isomeric with ethylenic oxide. The oxide has been prepared by the action of potash on the ethylenic hydrochloride. This compound breaks up into hydrochloric acid and ethylenic oxide—

$$C^2H^4\begin{matrix}Cl\\H\,O\end{matrix} = H\,Cl + C^2H^4O.$$

In this respect it differs from its prototype, sulphuric hydrochloride, which breaks up into sulphuric hydrate and sulphuric chloride.

Ethylenic oxide boils at 13.5°. By heating in a closed vessel with water it reproduces glycol. Some of the oxide combines in the process with water in the proportion of two molecules of ethylenic oxide to one of water, forming the compound $\begin{matrix}(C^2H^4)^2\\H^2\end{matrix}O^3$, called diethylenic glycol.

**302.** When ethylenic bromide is heated with glycol this same compound is obtained together with triethylenic glycol, $\begin{matrix}(C^2H^4)^3\\H^2\end{matrix}O^4$, tetrethylenic glycol, $\begin{matrix}(C^2H^4)^4\\H^2\end{matrix}O^5$, pentethylenic glycol, $\begin{matrix}(C^2H^4)^5\\H^2\end{matrix}O^6$, and hexethylenic glycol, $\begin{matrix}(C^2H^4)^6\\H^2\end{matrix}O^7$.

These **Polyethylenic Glycols** are analogous to glycol itself in their reactions. But the addition of each molecule of ethylenic oxide raises the boiling-point of the glycol.

Propylenic bromide forms a glycol by the same processes which serve to prepare ethylenic glycol.

Propylenic hydrate $\left(C^3H^6\begin{matrix}H\\H\end{matrix}O\right)$ boils however at a lower temperature than ethylenic hydrate—viz. at 188°.

Butylenic glycol ($C^4H^{10}O^2$) boils still lower—viz. at 183° to 184°.

Amylenic glycol ($C^5H^{12}O^2$) boils lowest of the four—viz. at 177°.

Methylenic glycol ($CH^4O^2$) has not been obtained.

Methylenic acetate $\left(\begin{matrix}CH^2\\(C^2H^3O)^2\end{matrix}O^2\right)$ is obtained by the action of methylenic iodide on argentic acetate. It is decomposed by water into acetic acid and a solid body melting at 152° and isomeric with methylenic oxide—

$$\left(\begin{matrix}CH^2\\(C^2H^3O)\end{matrix}O^2\right)^2 + (H^2O)^2 = \begin{matrix}CH^2\\CH^2\end{matrix}O^2 + \left(\begin{matrix}C^2H^3O\\H\end{matrix}O\right)^2.$$

Ethylenic sulphhydrate $\left(\begin{matrix}C^2H^4\\H^2\end{matrix}S^2\right)$ was obtained many years ago by Löwig, by decomposing ethylenic bromide by an alcoholic solution of potassic sulphhydrate—

$$C^2H^4Br^2 + \begin{matrix}K^2\\H^2\end{matrix}S^2 = \begin{matrix}C^2H^4\\H^2\end{matrix}S^2 + (KBr)^2.$$

It combines readily with mercuric oxide, as the monatomic mercaptans do.

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# CHAPTER XLIX.

**303.** When cautiously oxidized, glycol gives rise to the formation of an acid called **Glycollic Acid.** The reaction is perfectly similar to the formation of acetic acid by the oxidation of alcohol—

$$\begin{matrix}C^2H^4\\H^2\end{matrix}O^2 + O^2 = \begin{matrix}C^2H^2O\\H^2\end{matrix}O^2 + H^2O.$$

Glycollic acid is also obtained by the action of potassic hydrate at a high temperature on potassic chloracetate—

$$KHO + \overset{K}{C^2H^2ClO}O = KCl + \overset{K}{C^2H^2(HO)O}O.$$

When potassic chloracetate is heated by itself anhydrous glycollic acid is formed—

$$C^2H^2ClKO^2 = ClK + C^2H^2O^2.$$

Glycollic acid is monobasic, forming only normal salts, such as $C^2H^3KO^3$, $Ba(C^2H^3O^3)^2$, &c.

When further oxidized glycol yields oxalic acid—

$$\overset{H^2}{C^2H^4}O^2 + O^4 = \overset{H^2}{C^2O^2}O^2 + (H^2O)^2;$$

and glycollic acid is easily oxidized, forming oxalic acid.

It is worthy of note that oxalic acid, having two atoms of oxygen in its radical ($C^2O^2$), is bibasic, whereas glycollic acid, having one atom of oxygen in its radical ($C^2H^2O$), is monobasic.

Under the influence of nascent hydrogen oxalic acid has been reduced to glycollic acid.

The two acids which stand to propylic glycol in the same relation as glycollic and oxalic acids stand to glycol, are lactic acid ($C^3H^6O^3$), homologous with glycollic, and malonic acid ($C^3H^4O^4$), homologous with oxalic acid.

**304. Lactic Acid** ($C^3H^6O^3$) has obtained its name from the circumstance of its being formed from the sugar of milk, by the spontaneous decomposition of milk when exposed to the air. Milk is well known to 'turn sour' on keeping, and at the same time to become thick by the formation of a solid precipitate of caseine. Lactic acid is present in many animal fluids.

It is most easily obtained in quantity by the lactic fermentation of sugar. This change takes place when sugar is dissolved in water and mixed with powdered cheese, the mixture being kept at a temperature of about 30°, and the free acid

neutralized in proportion as it is formed. The best way to keep the liquid neutral is to put into it zinc carbonate, when zinc lactate is formed, and can be purified by re-crystallization.

When carefully heated to 130° or 140° lactic acid decomposes in part, into water and anhydrous lactic acid ($C^3H^4O^2$). Some of this anhydrous acid decomposes into aldehyde and carbonic oxide ($C^3H^4O^2 = C^2H^4O + CO$).

Phosphoric chloride forms with lactic acid the lactic chloride $C^3H^4OCl^2$, and when partially decomposed by an alkaline hydrate this chloride forms a chloro-propionate—

$$C^3H^4OCl^2 + HKO = C^3H^4ClKO^2 + HCl.$$

By the action of nascent hydrogen the chlorine can be removed from this salt and replaced by hydrogen, forming a common propionate. Lactic acid is easily reduced to propionic acid by the action of strong hydriodic acid—

$$C^3H^6O^3 + (HI)^2 = C^3H^6O^2 + H^2O + I^2.$$

Acetonic acid ($C^4H^8O^3$) is in its composition homologous with lactic acid, but has not as yet been much studied. It is made by adding to acetone the elements of formic acid, by the action of hydrochloric acid on prussic acid in presence of water—

$$C^3H^6O + CNH + (H^2O)^2 + HCl = C^4H^8O^3 + ClNH^4.$$

Butylactic and oxibutyric acids are names given to acids of the same composition as acetonic acid.

Leucic acid ($C^6H^{12}O^3$) has been obtained from a crystalline amide called leucine by the action of nitrous acid.

A body of the same composition has been obtained by Frankland and Duppa from vinic oxalate. One atom of oxygen in the radical of the oxalate is replaced by two atoms of ethyle—

$$\frac{C^2O^2}{(C^2H^5)^2}O^2 + (C^2H^5)^2 - O = \frac{C^2(C^2H^5)^2O}{(C^2H^5)^2}O^2.$$

From this leucic ether other salts of the acid are prepared. A similar process has been applied by the same chemists to the preparation of other terms of the series, such as—

$$C^5H^{10}O^3 = \overset{H}{C^2(CH^3)(C^2H^5)}O\,O^2.$$

The substitutions are effected by the action of metallic zinc on oxalic ether mixed with vinic iodide or methylic iodide, &c., or a mixture of iodides. There are also some acids which differ from those of the aromatic series by containing one atom of oxygen in each molecule beyond the elements of the aromatic acids. These are—

Oxybenzoic acid ($C^7H^6O^3$).
Oxytolulic acid ($C^8H^8O^3$).
Phloretic acid ($C^9H^{10}O^3$).
Oxycuminic acid ($C^{10}H^{12}O^3$).

**305.** Another series of diatomic acids is the oxalic series. Each molecule of these acids forms two neutral salts with potassium, containing two atoms of the metal, and double salts containing an atom of hydrogen and an atom of potassium, having a decidedly acid reaction. The acids are accordingly considered as dibasic. These acids are:

Oxalic acid ($H^2C^2O^4$).
Malonic acid ($H^2C^3H^2O^4$).
Succinic acid ($H^2C^4H^4O^4$).
Lipic acid ($H^2C^5H^6O^4$).
Adipic acid ($H^2C^6H^8O^4$).
Pimelic acid ($H^2C^7H^{10}O^4$).
Suberic acid ($H^2C^8H^{12}O^4$).
Anchoic acid ($H^2C^9H^{14}O^4$).
Sebasic acid ($H^2C^{10}H^{16}O^4$).

Oxalic acid has been described among the simplest compounds of carbon. Malonic acid is but little known as yet. It has been obtained by the oxidation of malic acid, and by the action of caustic potash on cyanacetic acid—

$$C^2H^2\overset{K}{(CN)}O\,O + H^3KO^2 = \overset{K^2}{C^3H^2O^2}O^2 + NH^3.$$

**Succinic Acid** ($C^4H^6O^4$) is among the products of the dry distillation of amber. It is formed by the action

of nitric acid on acids of the adipic series, such as butyric acid—

$$C^4H^8O^2 + O^3 = C^4H^6O^4 + H^2O.$$

In many processes of fermentation it is one of the secondary products, and in the fermentation of a malate it is one of the chief products. It is formed by the action of hydriodic acid on tartaric acid—

$$C^4H^6O^6 + (HI)^4 = C^4H^6O^4 + (H^2O)^2 + I^4.$$

Also by the same treatment of malic acid—

$$C^4H^6O^5 + (HI)^2 = C^4H^6O^4 + (H^2O) + I^2.$$

Succinic acid has been built up from ethylene and cyanogen. Ethylenic cyanide is decomposed by potash, forming succinate—

$$C^2H^4(CN)^2 + (H^3KO^2)^2 = C^4H^4K^2O^4 + (NH^3)^2.$$

Succinic acid dissolves readily in water with a decidedly acid reaction. When heated it decomposes into water and anhydrous succinic acid—

$$C^4H^6O^4 = C^4H^4O^3 + H^2O.$$

Phosphoric chloride decomposes succinic acid, forming the anhydrous acid, hydrochloric acid, and phosphoric oxychloride. A further action of phosphoric chloride decomposes the anhydrous acid, forming succinic chloride—

$$C^4H^4O^3 + PCl^5 = C^4H^4O^2Cl^2 + POCl^3.$$

Calcic succinate ($C^4H^4CaO^4$) is soluble in water. The hydrocalcic succinate ($CaH^2(C^4H^4O^4)^2$) is a crystallizable salt.

Barytic succinate ($C^4H^4BaO^4$) is but slightly soluble in water, and it is insoluble in a mixture of ammonia and alcohol.

Ferric succinate is insoluble in water but soluble in acids.

Succinic ether is decomposed by ammonia, forming succinamide—

$$C^4H^4(C^2H^5)^2O^4 + (NH^3)^2 = C^4H^4O^2(NH^2)^2 + \\ + (C^2H^6O)^2.$$

There is also an acid called succinamic acid, derivable by a similar reaction from hydrovinic succinate—

$$C^4H^4O^2\begin{matrix}H\\C^2H^5\end{matrix}O + NH^3 = C^4H^4O^2\begin{matrix}H\\NH^2\end{matrix} + C^2H^6O.$$

Anhydrous succinic acid combines with ammonia, forming a compound in which the radical succinyle ($C^4H^4O^2$) replaces two atoms of hydrogen of the ammonia—

$$C^4H^4O^3 + NH^3 = NHC^4H^4O^2 + H^2O.$$

This compound is called succinimide. It dissolves readily in water and forms beautiful crystals.

Most of the higher terms of the oxalic series are made by the action of dilute nitric acid on acids of the adipic series or on oleic acid.

Sebasic acid is formed by the dry distillation of oleic acid, but the most ready way of obtaining it in quantity is by heating castor-oil soap with potassic hydrate. The soap contains an acid called ricinoleic acid, and this breaks up with the hydrate into sebate and a volatile alcohol. Sebasic acid is very slightly soluble in water, and can easily be obtained in crystals.

**306.** All these acids contain diatomic radicals—oxalyl ($C^2O^2$), malonyl ($C^3H^2O^2$), succinyl ($C^4H^4O^2$), &c.

These radicals form chlorides corresponding to the hydrates. Thus succinic chloride is $C^4H^4O^2Cl^2$. Oxalic acid forms, however, an exception in this respect, for by the action of phosphoric acid it is broken up into a mixture of carbonic acid and carbonic oxide, whilst hydrochloric acid and phosphoric oxy-chloride are formed.

These acids are formed on the type of two molecules of water $\left(\begin{matrix}H^2\\H^2\end{matrix}O^2\right)$, the radical replacing two atoms of hydrogen, one in each molecule, whilst imparting to the compounds sufficient acid power to react on two molecules of potassic hydrate,

and to neutralize the two atoms of alkali metal in the normal succinates, such as $\begin{matrix} C^4H^4O^2 \\ K^2 \end{matrix} O^2$.

In this respect the acids of the oxalic series differ from those of the lactic series. For although lactic acid contains the diatomic radical lactyl ($C^3H^4O$) in the place of two atoms of hydrogen of the double molecule $\left(\begin{matrix} H^2 \\ H^2 \end{matrix} O^2\right)$ thus, $\begin{matrix} C^3H^4O \\ H^2 \end{matrix} O^2$, it is only capable of reacting on one atom of potassic hydrate, forming the so-called normal lactate—

$$\begin{matrix} C^3H^4O \\ H\,K \end{matrix} O^2;$$

and if the second atom of typical hydrogen be expelled by the action of metallic potassium, the compound $\begin{matrix} C^3H^4O \\ K^2 \end{matrix} O^2$ is as alkaline as potassium alcohol $\left(\begin{matrix} C^2H^5 \\ K \end{matrix} O\right)$, and is decomposed even by water like potassium alcohol. The two atoms of typical hydrogen in each molecule of the acids of the lactic series are distinguished by the terms 'metallic hydrogen,' replaceable by metals, and 'alcoholic hydrogen,' or hydrogen only replaceable by metals in the same sort of way as the typical hydrogen of alcohol.

This difference of acid power in the two series is connected with the fact that acids of the oxalic series have got two atoms of oxygen in their radical, whereas the acids of the lactic series have only one atom of oxygen in their radicals. Glycols, and homologues which have no oxygen in their radicals, cannot neutralize even one atom of potassium when it replaces one of their atoms of typical hydrogen, as in the compound $\begin{matrix} C^2H^4 \\ H\,K \end{matrix} O^2$.

**307.** The chlorides or bromides of diatomic radicals react normally upon two molecules of ammonia as upon

two molecules of water. Thus ethylenic bromide, heated with ammonia, forms compounds called diamines, derived from two molecules of ammonia ($N^2H^2H^2H^2$) by the replacement of two atoms of hydrogen by one atom of ethylene, forming $N^2H^2H^2(C^2H^4)$; or by the replacement of four atoms of hydrogen by two atoms of ethylene, forming

$$N^2H^2(C^2H^4)(C^2H^4);$$

or by the replacement of the six atoms of hydrogen by three atoms of ethylene, forming $N^2(C^2H^4)(C^2H^4)(C^2H^4)$, called triethylene diamine. Each molecule of these diamines combines with two molecules of hydrochloric acid, forming salts such as $N^2H^4C^2H^4H^2Cl^2$, and these chlorides, in their turn, unite with platinic chloride, forming double chlorides, such as $\begin{matrix}N\\N\end{matrix}(C^2H^4)^3\begin{matrix}H\,Cl\\H\,Cl\end{matrix}PtCl^4$.

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# CHAPTER L.

**308. Glycerine** has been shewn by the classical investigations of Berthelot to be a triatomic alcohol; and its empirical formula ($C^3H^8O^3$) is written on the water-type as containing the triatomic radical glycerile ($C^3H^5$) in the place of three atoms of hydrogen.

Glycerine is now prepared on a large scale by the distillation of palm-oil and similar fats in superheated steam. The fat is decomposed, by the action of the steam, into glycerine and hydric palmitate, &c. Thus palmitine, in an excess of steam, takes up three molecules of water—

$$\begin{matrix}C^3H^5\\(C^{16}H^{31}O)^3\end{matrix}O^3 + (H^2O)^3 = \begin{matrix}C^3H^5\\H^3\end{matrix}O^3 + \left(\begin{matrix}H\\C^{16}H^{31}O\end{matrix}O\right)^3.$$

The products are condensed above 100°C; so that the excess of steam passes on, leaving the acids and the glycerine in

the condenser. Glycerine is also prepared by the action of litharge in presence of water upon fat. The glycerine can easily be washed away from the plaster which is formed, purified by sulphuretted hydrogen, and evaporated in a water-bath, to drive off the excess of water which is present. In this manner glycerine is obtained, in the form of a thick liquid of sweet but peculiar taste, soluble in water in all proportions, also soluble in alcohol, but insoluble in ether. Glycerine is decomposed at a high temperature, and one of the products formed is acroleine ($C^3H^4O$), a volatile liquid of most penetrating odour. Some of the glycerine evaporates in the products of decomposition of the remainder. Redtenbacher recommends heating glycerine, or a compound of glycerine, with hydropotassic sulphate, in order to detect glycerine by the odour of acroleine which is formed.

Hydrochloric acid decomposes glycerine in three successive stages—

$$C^3H^8O^3 + HCl = C^3H^7O^2Cl + H^2O.$$

This first compound is called monochlorhydrine. It is in its turn decomposed by hydrochloric acid, forming dichlorhydrine—

$$C^3H^7O^2Cl + HCl = C^3H^6OCl^2 + H^2O.$$

The further action of hydrochloric acid causes the dichlorhydrine to break up into hydrochloric acid and so-called epichlorhydrine—

$$C^3H^6OCl^2 = HCl + C^3H^5OCl.$$

Phosphoric chloride, however, forms the normal chlorhydrine—

$$C^3H^6OCl^2 + PCl^5 = C^3H^5Cl^3 + POCl^3 + HCl.$$

This chlorhydrine is the normal chloride of the triatomic radical glycerile. A corresponding bromide has been obtained; and from the bromhydrine Wurtz has reproduced glycerine by the action of argentic acetate, and the subsequent decomposition of the 'acetine' thus obtained.

Other monobasic acids act in a similar manner to hydrochloric. Thus a mixture of sulphuric acid with strong nitric acid transforms glycerine into a heavy oil—glyceric nitrate, or nitrine $\left(\begin{matrix}C^3H^5\\(NO^2)^3\end{matrix}O^3\right)$.

By acting upon glycerine by potassium its typical hydrogen can be partially replaced by the metal, and ethylic iodide replaces this potassium by ethyle.

**309.** By heating glycerine with acids of the acetic series Berthelot has prepared artificially a considerable number of fats. Thus on acetic acid glycerine reacts in three successive proportions—

$$C^3H^8O^3 + C^2H^4O^2 = C^3H^7O^2C^2H^3O^2 + H^2O;$$

$$C^3H^8O^3 + (C^2H^4O^2)^2 = C^3H^6O(C^2H^3O^2)^2 + (H^2O)^2;$$

$$C^3H^8O^3 + (C^2H^4O^2)^3 = C^3H^5(C^2H^3O^2)^3 + (H^2O)^3.$$

These compounds are called monacetine, diacetine, and triacetine. The compounds formed by the action of the higher acids of the series are perfectly analogous to them. In order to separate the fat from the excess of acid which was used in the operation, Berthelot acted upon the mixture by sodic carbonate, thereby dissolving out all the acid without decomposing the glycerine compound; and by dissolving the fat in ether he separated it from the free glycerine.

By the action of monochlorhydrine on sodic ethylate monethyl glycerine has been prepared—

$$C^3H^7O^2Cl + NaC^2H^5O = NaCl + \begin{matrix}C^3H^5\\H^2C^2H^5O^3\end{matrix}.$$

And in like manner dichlorhydrine reacts on two molecules of sodic ethylate, forming diethylic glycerine; and the triethyline has been obtained by the action of ethylic iodide on diethylsodic glycerine—

$$\begin{matrix}C^3H^5\\Na(C^2H^5)^2\end{matrix}O^3 + C^2H^5I = NaI + \begin{matrix}C^3H^5\\(C^2H^5)^3\end{matrix}O^3.$$

**310.** By the oxidation of glycerine an acid called glyceric acid, of the composition $C^3H^6O^4$, has been obtained.

Glyceric acid contains the triatomic radical $C^3H^3O$; but it appears to be monobasic, so that two of the typical atoms of hydrogen in it are considered as alcoholic hydrogen, while one only is metallic $\left(\begin{matrix}C^3H^3O\\H^2H\end{matrix}O^3\right)$.

An acid called tartronic acid has been obtained by the decomposition of nitrotartaric acid. Tartronic acid has the composition $C^3H^4O^5$; and Kekulé suggests that it may be the next product of the oxidation of glycerine, so that its rational formula would then be $\begin{matrix}C^3HO^2\\HH^2\end{matrix}O^3$.

Another acid, nearly related to these, is malic acid ($C^4H^6O^5$); an acid which occurs in gooseberries, rhubarb, sour apples, barberries, and many other vegetables; but which is most conveniently prepared from the juice of unripe mountain-ash berries.

**Malic Acid** is dibasic; but, as Kekulé suggests, its radical is probably triatomic, according to the formula $\begin{matrix}C^4H^3O^2\\HH^2\end{matrix}O^3$, according to which it is represented as homologous with tartronic acid, and is derived from butylic glycerine $\left(\begin{matrix}C^4H^7\\H^3\end{matrix}O^3\right)$.

Calcic malate ($CaC^4H^4O^5$) is insoluble in water. It dissolves in dilute nitric acid; and the double salt

$$H^2Ca(C^4H^4O^5)^2$$

crystallizes out easily from this solution.

Plumbic malate becomes semi-fluid and crystalline by heating in plumbic acetate.

Hydriodic acid reduces malic acid to succinic—

$$C^4H^6O^5 + (HI)^2 = C^4H^6O^4 + H^2O + I^2.$$

Malic acid rotates a polarized ray of light.

By the action of heat malic acid yields two acids, isomeric

with one another, and differing from it by containing the elements $H^2O$ less than malic acid in each molecule—

$$C^4H^6O^5 - H^2O = C^4H^4O^4.$$

These acids are called malic and fumaric. They combine with nascent hydrogen, forming succinic acid—

$$C^4H^4O^4 + H^2 = C^4H^6O^2.$$

Many vegetables contain a nitrogenized crystallizable compound called asparagine, which is represented by the formula $C^4H^4O^3(NH^2)^2$. Asparagine behaves as the amide of malic acid. By prolonged contact with hot water it is converted into the ammonia-salt of malamic acid—

$$C^4H^4O^3(NH^2)^2 + H^2O = NH^4C^4H^4O^4NH^2.$$

By the action of nitrous acid it is decomposed, yielding a kind of malic acid, which does not rotate light—

$$C^4H^4O^3(NH^2)^2 + N^2O^3 = C^4H^6O^5 + N^4 + (H^2O).$$

**311.** Amongst triatomic compounds Kekulé classes the so-called nitriles—bodies such as acetonitrile, &c., which are formed either by the combination of cyanogen with a monatomic alcohol radical or by the action of anhydrous phosphoric acid on the ammonia-salt of an acid of the acetic series.

It is not impossible that **Aniline-red** or **Rosaniline** may contain a tri-atomic radical. This beautiful base is usually made by the action of arsenic acid on a mixture of toluidine and aniline. Its formula ($C^{20}H^{19}N^3$) shews it to be a triamine. Its acetate ($C^{20}H^{19}N^3C^2H^4O^2$) crystallizes in magnificent crystals, shewing a greenish metallic lustre by reflected light. Its hydrochlorate ($C^{20}H^{19}N^3HCl$) crystallizes in needles.

Aniline blue ($C^{20}H^{16}(C^6H^5)^3N^3HCl$) is made by the action of aniline on the acetate of rosaniline. Ammonia is given off in the process, and three atoms of hydrogen are replaced in the red compound by the atoms of phenyl. The product acquires its characteristic blue colour by combination with hydrochloric acid.

Chrysaniline is the name given to a yellow compound, formed simultaneously with rosaniline by the action of arsenic acid on commercial aniline. It is extracted from the residues from which the rosaniline has been separated out. Its composition is represented by the formula $C^{20}H^{17}N^{3}$.

Another beautiful dye is the so-called mauveine ($C^{27}H^{24}N^{4}$), which was discovered by Mr. Perkin, and opened the field of investigation of these coloured derivatives of aniline and toluidine.

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# CHAPTER LI.

**312.** Tetratomic compounds are chiefly known among acids, but a crystallizable body called erithrite has been extracted from various lichens, and Berthelot has proved that it combines with fatty acids under similar circumstances to glycerine. The formula of erithrite is $C^{4}H^{10}O^{4}$, and it it is considered as a tetratomic alcohol of the formula $\begin{matrix} C^{4}H^{6} \\ H^{4} \end{matrix}O^{4}$.

Hydriodic acid decomposes it, with formation of butylic iodide ($C^{4}H^{9}I$).

**Tartaric Acid** ($C^{4}H^{6}O^{6}$) is classed by Kekulé as a tetratomic acid, and thus related to erithrite by replacement of four atoms of hydrogen in the radical $C^{4}H^{6}$ by two atoms of oxygen $\left(\begin{matrix} C^{4}H^{2}O^{2} \\ H^{4} \end{matrix}O^{4}\right)$.

Tartaric acid is contained in many vegetable juices. It is usually prepared from argol, the crude hydropotassic tartrate which collects from acid continental wines in the form

*of* a reddish crust. The salt is decomposed by boiling with chalk, forming a precipitate of calcic tartrate and a solution of potassic tartrate—

$$(C^4H^5KO^6)^2 + CaCO^3 = C^4H^4CaO^6 + \\ + C^4H^4K^2O^6 + CO^2 + H^2O.$$

The solution of the potassium salt is transformed into calcic tartrate by the action of calcic chloride—

$$C^4H^4K^2O^6 + CaCl^2 = C^4H^4CaO^6 + (KCl)^2.$$

The two portions of calcium-salt obtained by these operations are decomposed by dilute sulphuric acid, and the tartaric acid is usually evaporated in vacuum pans.

It is thus obtained in the form of clear crystals, which contain no water of crystallization. When heated these crystals become electrical, shewing two opposite electrical charges at two opposite angles. These polarities are reversed during the process of cooling.

Tartaric acid dissolves readily in water, and its solution has a powerfully acid reaction. It is very liable to become mouldy, and to decompose on keeping. The aqueous solution of tartaric acid is dextrorotatory.

If present in sufficient quantity with a salt of a heavy metal, tartaric acid prevents the precipitation of the metallic oxide by potash. Alkaline solutions thus formed allow the heavy metal to be precipitated by sulphuretted hydrogen. This property is however not by any means characteristic of tartaric acid, as it belongs equally to many other polybasic acids.

**313.** Tartaric acid is decomposed by heat, and the odour of the products of its destructive distillation possesses some resemblance to that of burnt sugar, and is employed occasionally as a means of recognising the acid.

When the acid is cautiously heated it loses a molecule of water, forming anhydrous tartaric acid—

$$C^4H^6O^6 - H^2O = C^4H^4O^5;$$

and this anhydrous acid is capable of combining with the hydrate, forming so-called ditartaric acid. Among the products of the dry distillation of tartaric acid are pyruvic acid ($C^3H^4O^3$), and pyrotartaric acid ($C^5H^8O^4$). It is easy to account for the formation of these acids. Thus:

$$C^4H^6O^6 - CO^2 - H^2O = C^3H^4O^3, \text{ and}$$
$$(C^3H^4O^3)^2 - CO^2 = C^5H^8O^4.$$

Acetic acid accompanies these products.

When fused with potassic hydrate tartaric acid breaks up into an acetate and an oxalate—

$$C^4H^4K^2O^6 + KHO = C^2H^3KO^2 + C^2K^2O^4 + H^2O.$$

Tartaric acid is one of the best characterized bibasic acids. When half neutralised by potash it forms the slightly soluble hydropotassic tartrate commonly called cream-of-tartar. But when twice as much potash is added this salt is dissolved, with formation of the readily soluble normal tartrate—

$$C^4H^4K^2O^6.$$

When lime-water is added gradually to a solution of the acid no precipitate is produced so long as the liquid is acid, but as soon as it becomes neutral a white precipitate of normal calcic tartrate is formed. This salt dissolves in cold potash, but is precipitated by boiling. It dissolves also in ammonia chloride.

Sodium forms a normal tartrate and a double tartrate with hydrogen. This hydrosodic tartrate is an exceedingly convenient reagent for the separation of potassium and sodium, as it precipitates concentrated solutions of potassium salts and has no action on sodium salts.

Rochelle salt is the name given to sodiopotassic tartrate, a salt which crystallizes in singularly well-formed crystals.

Tartaric acid is readily oxidized by nitric acid. It also reduces metallic silver from its salts. One of the commonest salts of tartaric acid is the so-called tartar-emetic, potassio-antimonic oxitartrate ($C^4H^4KSbO^7$). The salt is usually

prepared by boiling pure antimonic oxide with hydropotassic tartrate. It may be considered as containing the monatomic radical Sb O in place of one atom of hydrogen of the original tartrate.

**314.** Racemic acid is isomeric with common tartaric acid. It has no rotating action on a polarized ray of light. Its solution causes a precipitate when added to a solution of calcic chloride, and racemic acid is thus distinguished from tartaric acid. Pasteur has shewn that racemic acid is a compound of tartaric acid (dextrorotatory) with an isomeric acid which he calls levorotatory tartaric acid. The two are separated by crystallizing a solution of ammonio-sodic racemate. Two varieties of crystals are formed, each of them hemihedral, but one having the opposite modifications to the other; so that if a model of one of these crystals were made of cardboard it would represent the other variety when turned inside out.

Tartaric and racemic acids are formed by the cautious oxidation of saccharic and mucic acids by nitric acid. They are, in their turn, easily reduced by nitric acid, forming oxalic acid and ultimately carbonic acid. Tartaric acid also reduces metallic silver from solutions of its salts.

Homotartaric acid is the name given by its discoverer, Kekulé, to an acid of the composition $C^5 H^8 O^6$, formed by the action of argentic hydrate on the compound of bromine with itaconic acid. This compound is homologous with dibromo-succinic, and is called dibromopyro-tartaric acid—

$$C^5 H^6 Br^2 O^4 + (Ag H O)^2 = (Ag Br)^2 + C^5 H^8 O^6.$$

**315. Citric Acid** ($C^6 H^8 O^7$) is usually prepared from lemon-juice. It is also contained in tamarinds, and in many other acid fruits.

The expressed juice is neutralized by lime, and the dry calcic citrate is imported into this country for the preparation of the

acid. The acid is prepared from this calcium salt by the action of sulphuric acid, very much in the same way as tartaric acid.

The acid crystallizes readily from water, and the crystals contain a molecule of water of crystallization.

Citric acid is tribasic, and its formula is written on the water-type as containing the triatomic radical $C^6H^4O^3$: thus, $\begin{matrix} C^6H^4O^3 \\ H\,H^3 \end{matrix} O^4$. It is thus considered to contain four atoms of typical hydrogen, three of which are metallic and replaceable by potassium, sodium, &c., while the fourth is called alcoholic hydrogen.

**Potassic Citrate** ($K^3C^6H^5O^7$), as well as hydrodipotassic citrate ($HK^2C^6H^5O^7$) and dihydropotassic citrate ($H^2KC^6H^5O^7$), are readily soluble in water; and citric acid can be distinguished from tartaric acid by the non-precipitation of potash by an excess of citric acid.

When lime-water is added gradually to an aqueous solution of citric acid a double salt is at first formed, but even when the acid is neutralized by the formation of the normal salt $Ca^3(C^6H^5O^7)^2$ no precipitate is formed in the cold. On boiling an alkaline mixture of citric acid and lime-water, the salt is precipitated.

When citric acid is cautiously heated it loses the elements of a molecule of water, forming aconitic acid ($C^6H^6O^6$); and when aconitic acid is heated to a still higher temperature than that at which it was formed, carbonic acid is given off, and an acid of the composition $C^5H^4O^4$ is formed. This acid is called itaconic acid. Citraconic acid, isomeric with itaconic, is formed at the same time, and a third isomeric is called mesaconic acid.

Pentatomic compounds are as yet but little known. Kekulé places, however, in this group two acids—aposorbic acid ($C^5H^8O^7$), a dibasic acid supposed to contain the pentato-

mic radical $C^5H^3O^2$. It was made by Dessaigues, by the action of nitric acid on sorbin. The other pentatomic acid is desoxalic ($C^5H^6O^5$), obtained by Löwig among the products of the action of sodium on oxalic ether. Desoxalic acid is supposed to contain the radical $C^5H^6O^3$, and it is tribasic. It breaks up when heated into carbonic acid and racemic acid—

$$C^5H^6O^5 = C^4H^6O^6 + CO^2.$$

**316. Mannite** ($C^6H^{14}O^6$) is a hexatomic alcohol, containing the radical $C^6H^8$ in the place of 6 atoms of hydrogen in 6 molecules of water $\left(\begin{matrix}C^6H^8\\H^6O^6\end{matrix}\right)$.

It is contained in manna, and is frequently formed from sugar by a process of fermentation. It has been made by the action of nascent hydrogen, evolved by sodium amalgam, on uncrystallizable sugar. It is readily soluble in water, but far less soluble in alcohol. It melts between 160° and 165°, and boils, with partial decomposition, at 200°.

Mannite reduces gold and silver from aqueous solutions of their salts, but it does not reduce copper from cupric oxide in presence of free potash.

It combines with stearic acid, &c. in the same sort of way as glycerine, and Berthelot has obtained mannitic tetrahydric distearate and mannitic dihydric tetrastearate.

Mannitic nitrate $\left(\begin{matrix}C^6H^8\\(NO^2)^6\end{matrix}O^6\right)$ is formed by the action of a mixture of strong nitric and sulphuric acid upon mannite. Sulphuretted hydrogen in presence of alcohol and ammonia reduces it to mannite. Hydriodic acid decomposes mannite, forming caproic iodide ($C^6H^{13}I$).

Mannitan ($C^6H^{12}O^5$) is formed by the removal of a molecule of water from mannite, by the action of heat.

Mannide ($C^6H^{10}O^4$) has been obtained by Berthelot by heating mannite to 200° or 250° with butyric acid.

Mannitic acid $\left(\begin{matrix}C^6H^6O\\H^6\end{matrix}O^6\right)$ is formed by the action of air on a mixture of platinum black and moist mannite. It is probably monobasic.

317. **Saccharic** and **Mucic Acid** $\left(\begin{matrix}C^6H^4O^2\\H^6\end{matrix}O^6\right)$ are formed by the action of dilute nitric acid on mannite. Saccharic acid is also formed by the first action of nitric acid on several kinds of sugar. It is most easily prepared from common cane-sugar. One part by weight of sugar is heated with three parts by weight of nitric acid, of density 1.25, and removed from the fire as soon as the action is fairly started. After the liquid has cooled down to about 50° it is kept at this temperature as long as any fumes are evolved. It is then diluted with half its volume of water, and half neutralized by potash. When allowed to stand for some days the liquid deposits crystals of hydropotassic saccharate—

$$\begin{matrix}C^6H^4O^2\\H^4HK\end{matrix}O^6.$$

Its normal potassium salt has the composition $\begin{matrix}C^6H^4O^2\\H^4K^2\end{matrix}O^6$. Saccharic acid has not been obtained in the crystalline state. When made from cane-sugar it is dextrorotatory. By the gentle action of nitric acid it forms dextrotartaric acid.

There are two ethers of saccharic acid corresponding to the potassium salts above-named, and an amide corresponding to the normal ether and obtained from it by the action of ammonia—

$$\begin{matrix}C^6H^4O^2\\H^4(C^2H^5)^2\end{matrix}O^6 + (NH^3)^2 = \begin{matrix}C^6H^4O^2\\H^4(NH^2)^2\end{matrix}O^4 + \left(\begin{matrix}H\\C^2H^5\end{matrix}O\right)^2.$$

Mucic acid, isomeric with saccharic, is formed by the action of nitric acid on milk-sugar, or gum-arabic. According to Pasteur it is best made from galactrose.

Mucic acid is easily deposited in the crystalline form from

its aqueous solution, for it is very slightly soluble in cold water. Like saccharic acid it is dibasic. On dry distillation it yields pyromucic acid—

$$C^6 H^{10} O^8 = C^5 H^4 O^3 + (H^2 O)^3 + C O^2.$$

Hydriodic acid reduces mucic acid, and, according to Crum-Brown, it appears that adipic acid is formed by the reduction—

$$C^6 H^{10} O^8 + (H I)^8 = C^6 H^{10} O^4 + (H^2 O)^4 + I^8.$$

Nitric acid oxidizes mucic acid, with formation of racemic acid; and this, in its turn, is subsequently oxidized to oxalic acid.

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# CHAPTER LII.

**318.** One of the most important families of organic bodies are the so-called carbonic hydrates; including sugars, gums, starch, woody fibre, &c. These bodies contain oxygen and hydrogen in the proportions in which they form water; or in other words, they contain twice as many atoms of hydrogen as of oxygen, but it is by no means probable that these elements are combined with one another in the form of water. They are probably related to alcohols in their composition, containing polyatomic radicals, such as $C^6 H^6$, in lieu of the hydrogen of water.

These compounds are classified by Kekulé under the three following formulæ, viz.

$$C^6 H^{12} O^6;$$
$$C^{12} H^{22} O^{11};$$
$$C^6 H^{10} O^5.$$

It may be, however, that some of them ought to be represented by multiples of these formulæ.

Grape-sugar, or dextrose, and uncrystallizable sugar are the two most important compounds having the formula $C^6 H^{12} O^6$. Galactose is also isomeric with them, and, like them, is capable of undergoing alcoholic fermentation under the action of yeast. These fermentable sugars are formed by the action of acids on compounds belonging to the other families of hydrocarbons. Thus dextrose is formed by boiling starch or dextrine with dilute sulphuric acid. It is also formed together with levulose by the action of dilute sulphuric acid on cane-sugar. Levulose is alone formed from inulin. And galactose is formed from milk-sugar by the action of dilute acids. These sugars are also formed from the same materials by the action of yeast. Thus cane-sugar in a fermenting fluid takes up the elements of water and forms a molecule of dextrose and a molecule of levulose. Dextrose is best obtained from so-called candied honey, i. e. honey which has deposited crystals by long standing. The syrup is drained from these crystals by allowing them to lie on a porous tile. They are then dissolved by the aid of heat in spirits of wine, and crystallized.

Dextrose dissolves in about an equal weight of water, and its solution is not decomposed by dilute sulphuric acid. It reduces ferric salts to ferrous salts, and reduces metallic silver from many of its solutions. It dissolves cupric hydrate in presence of caustic potash, and the solution deposits cuprous hydrate when gently heated. A lime compound is obtained by dissolving calcic hydrate in a solution of dextrose, and then adding alcohol. Its composition is represented by the formula—

$$C^6 H^{10} Ca O^6 H^2 O.$$

Dextrose also combines with common salt. There are three crystallizable compounds, but the one most easily

obtained consists of two molecules of dextrose combined with one molecule of salt and one of water—

$$(C^6H^{12}O^6)^2\,Cl\,Na\,H^2O.$$

**319.** Compounds of glucose with acids are called **Glucosates.** Many of them, such as tannin, amygdalin, salicin, &c., occur in the vegetable kingdom.

These bodies are decomposed in a manner which may be compared to the decomposition of fats by water. Thus, when boiled with a dilute mineral acid tannin takes up the elements of water, and decomposes into glucose and gallic acid—

$$\underbrace{C^{27}H^{22}O^{17}}_{\text{Tannin.}} + (H^2O)^4 = \underbrace{(C^7H^6O^5)^3}_{\text{Gallic Acid.}} + \underbrace{C^6H^{12}O^6}_{\text{Glucose.}}.$$

In like manner salicin breaks up into saligenine and glucose—

$$\underbrace{C^{13}H^{18}O^7}_{\text{Salicin.}} + H^2O = \underbrace{C^7H^8O^2}_{\text{Saligenine.}} + \underbrace{C^6H^{12}O^6}_{\text{Glucose.}}.$$

The decomposition of amygdaline is more complicated. It takes place in presence of certain ferments, forming benzoic aldehyde, prussic acid, and glucose—

$$C^{20}H^{27}NO^{11} + (H^2O)^2 = C^7H^6O + CNH + (C^6H^{12}O^6)^2.$$

Berthelot has prepared several glucosates by heating glucose with hydrated organic acids. Acetic glucosate was obtained by heating glucose for about 50 hours to 100° with acetic acid. It contains six atoms of acetyl, thus—$(C^6H^4(C^2H^3O)^6O^5)$, and the glucose lost a molecule of water at the same time, forming glucosan $(C^6H^{10}O^5)$, of which, properly speaking, this compound is the acetate. Similar compounds have been obtained with butyric and stearic acids, containing in one molecule two atoms of the radicals of these acids.

**Levulose** is not easily obtained in a state of purity, as dextrose, which usually accompanies it in sweet fruits, can only be separated approximatively from it by alcohol. In

contact with nascent hydrogen, evolved by sodium, levulose takes up hydrogen and is converted into mannite, a property which dextrose does not seem to possess—

$$\underbrace{C^6H^{12}O^6}_{\text{Levulose.}} + H^2 = \underbrace{C^6H^{14}O^6}_{\text{Mannite.}}.$$

It is less rapidly decomposed by yeast than dextrose; and accordingly a mixture of the two, such as is formed by boiling common sugar with dilute sulphuric acid, becomes more and more levorotatory up to a certain point, in proportion as the dextrose is broken up.

Its compound with lime is less soluble in water than the compound containing dextrose.

In order to separate levulose from dextrose Dubrunfaut recommends that 10 parts of so-called inverted sugar be mixed with 6 parts of calcic hydrate and 100 of water. After the mixture has been shaken for some time a deposit is formed, containing levulose combined with lime. Oxalic acid liberates the levulose from this compound.

Galactose is obtained by boiling milk-sugar with very dilute sulphuric acid. It has much resemblance to glucose, but, unlike glucose, it does not combine with salt.

**320. Sugar** ($C^{12}H^{22}O^{11}$), called by way of distinction cane-sugar, is found in the juices of many plants. It is mostly prepared from the juice of the sugar-cane, but on the continent of Europe it is prepared from beet-root. The manufacture of sugar from the sugar-cane is divided into two distinct operations: first, the preparation of a crude sugar in the neighbourhood in which the sugar is grown; and, secondly, the purification of the crude sugar by the so-called process of refining—an operation which is only performed with advantage in or near some large town, where skilled labour is abundant.

The freshly-cut sugar-canes are first passed through

rollers, which press out the greater part of the juice; and this juice is rapidly evaporated down after the neutralization of its acidity by lime. The mother-liquid drained off from the crystals of sugar is known by the name of molasses, or treacle.

The refining of sugar is effected by dissolving it in water and depriving it of its colouring matter by animal charcoal and albumen (from ox blood). The solution is evaporated in so-called vacuum pans—large boilers in which the syrup is boiled down—by the aid of a partial vacuum kept up by a powerful air-pump. The lower temperature at which ebullition thus takes place saves the sugar from the partial decomposition which it would undergo if boiled for an equal length of time under the atmospheric pressure.

When allowed to crystallize slowly sugar is obtained in the form of very hard and regular crystals, which are known by the name of sugar-candy. For most purposes the consumers prefer to use sugar in very small crystals, and to obtain it in that form the crystallization is disturbed by agitation of the liquid. A thick magma is thus obtained, which is poured into moulds, where the little crystals are cemented together by the deposition of more sugar between them, and assume the form of a sugar-loaf.

Sugar has a density of 1.6. It dissolves in about one-third of its weight of cold water, and in still less hot water, and the solution is dextrorotatory. It is not soluble in ether or in cold alcohol. It melts at 160°, and becomes coloured when heated to a higher temperature. It is completely destroyed by dry distillation.

**321.** Dilute mineral acids transform sugar, with assimilation of water, into a mixture of dextrose and levulose. Yeast effects the same transformation, and these products necessarily precede the formation of alcohol and the other products of vinous fermentation.

Sugar holds cupric oxide in solution in presence of caustic potash, and cuprous oxide is deposited very slowly indeed from this solution on the application of heat. With dilute nitric acid it forms saccharic and oxalic acids when heated. Caustic potash has very little action on sugar even at 100°, and serves to distinguish it from dextrose and levulose.

A solution of sugar is precipitated by baryta, the compound $C^{12}H^{22}O^{11}BaO$ being formed.

Lime dissolves very freely in syrup, forming various compounds.

The compound $C^{12}H^{22}O^{11}CaO$ is obtained by dissolving lime in aqueous solutions of sugar, taking care to keep the sugar in slight excess, and then adding alcohol to the solution. The compound is thus precipitated.

$C^{12}H^{22}O^{11}Ca^2O^2$ is obtained by saturating a solution of sugar with lime, by digesting it with an excess of the base, and then precipitating the filtered liquid by alcohol.

$C^{12}H^{22}O^{11}Ca^3O^3$ is precipitated by boiling an aqueous solution of sugar previously saturated with lime.

**Milk-sugar** ($C^{12}H^{22}O^{11}$) is obtained by evaporating to crystallization the clear liquid called whey, obtained by allowing skimmed milk to remain in contact with rennet until all the casein is deposited from it. The crystals first obtained can be purified by the action of animal charcoal and re-crystallization. When dried at 100° milk-sugar contains a molecule of water of crystallization, which can be expelled at 140°C. The crystals $C^{12}H^{22}O^{11}H^2O$ require about six times their weight of cold water for their solution; but they dissolve in twice their weight of boiling water. They are remarkably insipid; but the aqueous solution has a very sweet taste. It is dextrorotatory.

Dilute mineral acids convert grape-sugar into galactose, and yeast probably effects the same transformation before alcoholic fermentation sets in.

Cheese transforms milk-sugar into lactic acid, alcohol and carbonic acid being formed in small quantity at the same time.

Milk-sugar holds cupric oxide in solution in presence of potash; and the solution readily deposits cuprous oxide even in the cold.

Dilute nitric acid oxidizes milk-sugar, with formation of mucic acid.

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# CHAPTER LIII.

**322. Dextrine** ($(C^6H^{10}O^5)^n$) is a neutral and insipid body, used in the impure state under the name of British gum. It is obtained by heating starch to about 160°. The starch is sometimes moistened with exceedingly dilute nitric acid before heating. Dextrine is also formed from starch by the action of certain ferments. It is named from its powerfully dextrorotatory action on light. It dissolves in water, but not in alcohol or ether. It does not reduce cupric oxide when boiled with it in an alkaline liquid. Dilute mineral acids transform dextrine into dextrose. Nitric acid does not form mucic acid on oxidizing it.

Gum Arabic, or tree gum, has the same empirical composition as dextrine. Its aqueous solution is levorotatory. Moderately strong nitric acid oxidizes gum Arabic, with formation of mucic acid.

Other members of this same natural family are—

Lichenine, which is extracted by boiling water from Iceland moss. Its solution gelatinizes on cooling.

Inuline, prepared from dahlia roots.

Glycogen, discovered by Bernard in the liver.

**Starch** ($(C^6H^{10}O^5)^n$) is contained in many vegetables, in

the form of granules varying in size according to the vegetable from which it is obtained. Thus the granules of potato-starch have a diameter of nearly 0.2 millimeters, whilst those from Indian-corn have only a diameter of 0.05, and those from the seed of cheropodium quinoa have a diameter of about 0.002.

Starch is usually prepared from potatoes or rice. The granules are washed out from the fibrous substances in which they are interspersed, and they collect at the bottom of vessels in which the water is allowed to stand. Dilute caustic soda is used to dissolve out from the starch the albuminous matter with which it is at first mixed, and which would cause its decomposition if left in it.

Starch is not, properly speaking, soluble in water; but when it is heated to about 80° with water the granules swell up and burst, forming a paste. When long boiled in water starch passes over into a soluble substance usually called soluble starch. This soluble compound is exceedingly dextrorotatory. It is precipitated by alcohol in the form of a white powder, but retains its solubility in water.

Granulous starch and soluble starch are characterized by the deep blue colour of the compound which each of them forms with iodine.

Starch granules are dissolved by caustic potash, forming a liquid which has no rotatory action on a ray of light.

Dilute acids, as well as diastase, and some other ferments, dissolve starch by transforming it into a mixture of dextrine and dextrose. Starch is not dissolved by ammonia cuprate.

**323. Cellulose,** or **Woody fibre** ($(C^6H^{10}O^5)_n$), are the names usually given to the most insoluble bodies of this class. They are not soluble in water, nor in dilute caustic potash. Ammonia cuprate dissolves woody fibre. The material is most easily obtained in a state of purity from fresh and

picked cotton fibre. Caustic potash, alcohol, and ether are used successively to dissolve out foreign substances adhering to the fibres; and they are then very carefully washed and dried. Woody fibre immersed for some time in a concentrated solution of potash appears to combine with the alkali, and to form a compound containing two atoms of potassium to twenty-four atoms of carbon—

$$C^{24}H^{40}O^{20}K^2O.$$

Water dissolves out all the potash from this compound, reproducing woody fibre. Strong sulphuric acid combines with cellulose, forming a conjugated acid, analogous to sulphovinic acid.

When paper is immersed for a short time in a mixture of two volumes oil of vitroil and one of water, and thoroughly cleansed by repeated washings with water, and ultimately with ammonia, it is changed into a substance possessing considerable resemblance to parchment, and usually called 'vegetable parchment.' Strong nitric acid combines with woody fibre, forming products of substitution of $NO^2$ for hydrogen in the cotton. A mixture of strong nitric and sulphuric acids replaces three atoms of hydrogen by $(NO^2)^3$ in the group $C^6H^{10}O^5$, and the compound $C^6H^7(NO^2)^3O^5$ is the valuable explosive material called gun-cotton. A variety of nitrocellulose containing a smaller proportion of the radical $NO^2$ is used for the preparation of collodion, which is a solution of it in ether and a little alcohol. The gun-cotton ($C^6H^7(NO^2)^3O^5$) does not dissolve in ether and alcohol, but it dissolves in acetic ether. An alcoholic solution of potassic sulph-hydrate decomposes these bodies, reproducing woody fibre from all of them.

Strong sulphuric acid dissolves cellulose, transforming it into a substance analogous to starch, insoluble in water, but swelling up by contact with it, and becoming blue when placed in contact with iodine. By longer action of the

sulphuric acid a substance very much like dextrine is formed. When this dextrine from woody fibre is boiled with dilute sulphuric acid it is converted into dextrose.

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## CHAPTER LIV.

**324. Uric Acid** ($C^5H^4N^4O^3$) is in its constitution related to urea. It occurs sometimes in human urine, and if present in considerable quantity gives rise to the formation of concretions in the bladder and in other organs.

It is most easily obtained in a pure state from the urine of the boa-constrictor or other large serpents. This substance resembles chalk in its appearance, and consists chiefly of uric acid and ammonia. Dilute caustic potash dissolves the uric acid from it at a boiling heat, evolving ammonia. The solution contains potassic urate, $C^5\frac{H^2}{K^2}N^4O^3$—a salt of exceedingly alkaline properties. There is in the solution some colouring matter, which is most easily separated from the acid by passing carbonic acid through the impure solution of the potash salt. A double salt is thus precipitated (hydropotassic urate, $C^5\frac{H^3}{K}N^4O^3$), while the colouring matter remains mostly dissolved in the alkaline carbonate. By repeatedly dissolving in potash and reprecipitating by carbonic acid a colourless urate is at last obtained, from which uric acid is precipitated in the form of a white crystalline powder by dilute hydrochloric or sulphuric acid.

Uric acid requires about 18,000 parts of cold water for its solution. It is insoluble in alcohol and ether.

On dry distillation it is entirely decomposed, forming

amongst other products cyanuric acid, urea, ammonia cyanide, &c.

Its potash salts are more soluble in water than its soda salts, and lithia dissolves it even more freely than potash. Its compounds with the alkaline earths and the heavy metallic oxides are nearly insoluble in water. Uric acid is detected by the bright red colour which is formed when crystals of uric acid are moistened with nitric acid, dried by the aid of gentle heat, and then moistened with ammonia. This reaction is due to the formation of murexide.

Another way of detecting uric acid, described by Schiff, is to dissolve the acid in sodic carbonate and drop the solution onto paper moistened by silver nitrate. A brown colour is produced, owing to the reduction of silver.

**325.** The derivatives obtained from uric acid by the action of various reagents are exceedingly numerous. A few only of them can be here mentioned.

Alloxan ($C^4H^2N^2O^4$) is formed by the action of various oxidizing agents, such as nitric acid or chloric acid. Urea is formed at the same time thus—

$$\underbrace{C^5H^4N^4O^3}_{\text{Uric acid.}} + O + H^2O = \underbrace{C^4H^2N^2O^4}_{\text{Alloxan.}} + \underbrace{CH^4N^2O}_{\text{Urea.}}.$$

Alloxantin ($C^8H^4N^4O^7$) is formed by the action of reducing agents on alloxan, such as sulphuretted hydrogen, sulphurous acid, &c.—

$$\underbrace{(C^4H^2N^2O^4)^2}_{\text{Alloxan.}} + H^2 = \underbrace{C^8H^4N^4O^7}_{\text{Alloxantin.}} + H^2O.$$

Dialuric acid ($C^4H^4N^2O^4$) is formed by the further action of reducing agents with the aid of heat—

$$\underbrace{C^4H^2N^2O^4}_{\text{Alloxan.}} + H^2 = \underbrace{C^4H^4N^2O^4}_{\text{Dialuric acid.}}.$$

Parabanic acid ($C^3H^2N^2O^3$) is formed by the action of oxidizing agents, such as nitric acid, on alloxan—

$$\underbrace{C^4H^2N^2O^4}_{\text{Alloxan.}} + O = \underbrace{C^3H^2N^2O^3}_{\text{Parabanic acid.}} + CO^2.$$

Alloxantic acid ($C^4H^4N^2O^5$) is formed by the action of bases on alloxan. Its barium salt ($C^4H^2BaN^2O^5$) is decomposed by boiling into urea and the baryta salt of mesoxalic acid—

$$\underbrace{C^4H^2BaN^2O^5}_{\text{Baryta alloxanate.}} + H^2O = \underbrace{C^3BaO^5}_{\text{Baryta mesoxalate.}} + \underbrace{CH^4N^2O}_{\text{Urea.}}.$$

Parabanic acid undergoes decompositions analogous to those of alloxan, and it may be considered as a kind of alloxan containing the elements CO less than alloxan itself. Thus—

Oxaluric acid ($C^3H^4N^2O^4$) is obtained in combination with ammonia by the action of that base on parabanic acid. And oxalurates decompose when boiled into urea and corresponding oxalates.

The formation of oxaluric acid from parabanic acid is similar to that of alloxantic acid from alloxan. It differs from alloxantic acid in composition by the elements CO. When boiled with a mineral acid a solution of parabanic acid decomposes into oxalic acid and urea—

$$C^3H^2N^2O^3 + (H^2O)^2 = C^2H^2O^4 + CH^4N^2O;$$

oxaluric acid being no doubt first formed.

The two acids yield urea, while alloxantic acid yields a mesoxalate ($C^3O^5Ba$), and oxaluric acid yields an oxalate ($C^2O^4Ba$); and the mesoxalate has the same CO beyond the elements of the oxalate which alloxantic acid has beyond the elements of the oxaluric acid.

**326.** Mesoxalic and oxalic acids may with advantage

be compared to carbonic acid, as oxalic acid contains C O in addition to the elements of carbonic acid. Thus —

| $CO^3H^2$ | $C^2O^4H^2$ | $C^3O^5H^2$ |
|---|---|---|
| Carbonic. | Oxalic. | Mesoxalic. |

If we represent these acids on the type of two molecules of water $\left(\begin{matrix}H^2\\H^2\end{matrix}O^2\right)$ we have the series $\begin{matrix}CO\\H^2\end{matrix}O^2$, $\begin{matrix}C^2O^2\\H^2\end{matrix}O^2$, $\begin{matrix}C^3O^3\\H^2\end{matrix}O^2$; containing the radicals C O (carbonyl), $C^2O^2$ (oxalyl), and $C^3O^3$ (mesoxalyl). If, as Kekulé has suggested, carbonic acid be represented as derived from methylenic glycol $\left(\begin{matrix}CH^2\\H^2\end{matrix}O^2\right)$ by the replacement of $H^2$ by O, while glycollic acid in like manner is derived from ethylenic glycol $\left(\begin{matrix}C^2H^4\\H^2\end{matrix}O^2\right)$ by the same substitution, and oxalic acid by the replacement of the four atoms of hydrogen in the glycol by two atoms of oxygen, then mesoxalic acid will be derived from propylenic glycol $\left(\begin{matrix}C^3H^6\\H^2\end{matrix}O^2\right)$ by the replacement of the six atoms of hydrogen in the radical by three atoms of oxygen, lactic acid $\left(\begin{matrix}C^3H^4O\\H^2\end{matrix}O^2\right)$ and matonic acid $\left(\begin{matrix}C^3H^2O^2\\H^2\end{matrix}O^2\right)$ being the first two products of the oxidation.

**327.** An aqueous solution of alloxan decomposes on keeping, but more rapidly on boiling, into alloxantin, parabanic acid, and carbonic acid—

$$\underbrace{(C^4H^2N^2O^4)^3}_{\text{Alloxan.}} = \underbrace{C^8H^4N^4O^7}_{\text{Alloxantin.}} + \underbrace{C^3H^2N^2O^3}_{\text{Parabanic acid.}} + CO^2$$

Alloxantin can also be obtained by the action of sulphuretted hydrogen in the cold on an aqueous solution of alloxan—

$$(C^4H^2N^2O^4)^2 + H^2S = C^8H^4N^4O^7 + H^2O + S.$$

Nitric acid easily reverses this action and oxidizes alloxantin, with formation of alloxan.

Dialuric acid ($C^4H^4N^2O^4$) is formed by the reduction of alloxantin by sulphuretted hydrogen, or by sodium-amalgam. It can also be obtained by adding baryta-water to a solution of alloxantin, and boiling the violet precipitate which is first formed. The baryta salt of alloxantic and dialuric acids are thus formed—

$$(C^8H^4N^4O^7)^2 + H^2Ba^3O^4 = \underbrace{(C^4H^2BaO^5)^2}_{\text{Alloxantate.}} + (C^4H^3N^2O^4)^2Ba.$$

Alloxantin is accordingly built up of alloxan and dialuric acid with elimination of water—

$$\underbrace{C^4H^2N^2O^4}_{\text{Alloxan.}} + \underbrace{C^4H^4N^2O^4}_{\text{Dialuric acid.}} = \underbrace{C^8H^4N^4O^7}_{\text{Alloxantin.}} + H^2O.$$

By the action of oxidizing agents dialuric acid is transformed into alloxan.

Murexide ($C^8H^8N^6O^6$) is the name given to a beautiful compound, of red colour by transmitted light, and of which the crystals have a green colour and metallic lustre when seen by reflected light.

Murexide is considered as the ammonium salt of a peculiar acid called purpuric acid, and is represented by the rational formula $C^8H^4(NH^4)N^5O^6$. It is formed by the action of ammonia or its carbonate on a hot solution of alloxantin or of alloxan.

It is also said to be formed by the action of ammonia upon dry alloxantin heated to 100°C.

Several other salts of purpuric acid have been prepared, such as $C^8H^4KN^5O^6$, a deep red powder, and

$$Ba(C^8H^4N^5O^6)^2.$$

**328.** It appears from the elaborate investigations of

Bayer that dialuric acid and alloxantic acid are products of oxidation of an acid of the composition $C^4H^4N^2O^3$, which he calls barbituric acid. That able chemist represents dialuric acid as barbituric acid, in which an atom of hydrogen is replaced by (H O), as seen by the formula

$$C^4H^3(HO)N^2O^3;$$

and alloxantic acid will then be $C^4H^2(HO)^2O^3$.

The amide of cyanic acid ((C N) N $H^2$) may be represented as the hydride of a radical ((C $N^2$ H) H), and if this radical replace one atom of hydrogen in a molecule of barbituric acid, we have the formula—

$$C^4H^3(CN^2H)N^2O^3 = C^5H^4N^4O^3,$$

containing the elements of uric acid.

Allantoine ($C^4H^6N^4O^3$) is a compound which crystallizes in transparent prisms, and was named from its occurrence in the allantoic fluid of cows. It is formed by the action of plumbic peroxide on uric acid. Water containing uric acid in suspension is heated to the boiling-point, and the peroxide is thrown into the mixture in small quantities as long as it continues to lose its brown colour. The liquid thus obtained is filtered, treated with sulphuretted hydrogen, and evaporated to crystallization. Allantoine combines with silver, forming the compound $C^4H^5AgN^4O^3$.

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# CHAPTER LV.

**329. Guanin** ($C^5H^5N^5O$) is a feeble base found in guano. For its preparation guano should be boiled with milk of lime, and the solution filtered off from the residual solid matter, as often as a repetition of the process serves to

dissolve out any colouring matter. Uric acid and guanin are thus left undissolved, while most of the other substances which accompany them in the guano are dissolved out.

Guanin dissolves in boiling hydrochloric acid, and can thus be separated from the greater part of the uric acid. It can be precipitated by ammonia from a solution of its hydrochlorate ($C^5H^5N^5O\,H\,Cl$), and is insoluble in water.

By the action of a mixture of hydrochloric acid and potassic chlorate it is oxidized, with formation of parabanic acid and guanidin—

$$\underbrace{C^5H^5N^5O}_{\text{Guanin.}} + O^3 + H^2O = \underbrace{C^3H^2N^2O^3}_{\text{Parabanic acid.}} + \underbrace{CH^5N^3}_{\text{Guanidin.}} + CO^2.$$

Guanidin ($CH^5N^3$) is a strong base which dissolves readily in water, and absorbs carbonic acid from the air. Its carbonate ($CO^3H^2(CH^5N^3)^2$) crystallizes from water, but is insoluble in alcohol. Its platinum salt has the composition $PtCl^6(CH^5N^3)^2H^2$.

**330. Xanthin**, or xanthic oxide ($C^5H^4N^4O^2$), was found in an urinary calculus. It has since been found in flesh. It is also formed by the action of nitrous acid on guanin—

$$\underbrace{C^5H^5N^5O}_{\text{Guanin.}} + NO^2H = \underbrace{C^5H^4N^4O^2}_{\text{Xanthin.}} + N^2 + H^2O.$$

It is almost insoluble in cold water, and very slightly soluble in boiling water. It combines both with acids and bases, forming crystalline salts.

Another compound intimately related to xanthin in composition is

**Sarkine** ($C^5H^4N^4O$). It is a weak base, which has been found in flesh, also in blood, the liver, &c. It requires about 300 times its weight of cold water for its solution, but only

78 times its weight of boiling water. It differs in composition from uric acid by containing two atoms of oxygen less than uric acid contains, while xanthin stands between the two in composition.

A group of compounds related to uric acid and to guanin by their decompositions is formed of creatine and creatinine, together with their homologues glycocyamine and glycocyamidine.

**331.** Glycocyamine ($C^3H^7N^3O^2$) is formed by the action of glycocoll on an aqueous solution of cyanamide—

$$C^2H^5NO^2 + CN^2H^2 = C^3H^7N^3O^2.$$

Glycocoll. Cyanamide. Glycocyamine.

The compound crystallizes out from the mixture after a few days' standing. It requires 126 times its weight of cold water for its solution, but dissolves much more readily in hot water. Alcohol does not dissolve it. It forms a crystalline hydrochlorate ($C^3H^7N^3O^2HCl$) and a platinum-salt of the composition $PtCl^6H^2(C^3H^7N^3O^2)^2$.

When heated to 160°C in a current of hydrochloric acid gas, glycocyamine loses the elements of water and takes up those of hydrochloric acid. The compound thus obtained is the hydrochlorate of glycocyamidine—

$$C^3H^7N^3O^2 + HCl - H^2O = C^3H^5N^3OHCl.$$

From this hydrochlorate the base glycocyamidine ($C^3H^5N^3O$) can be liberated by plumbic oxide.

Glycocyamidine forms with zinc chloride a compound which crystallizes in needles, and is but slightly soluble in water.

**332.** Creatine ($C^4H^9N^3O^2$) is contained in the juices of flesh. It has also been found in the brain, and in urine. For its preparation lean meat should be finely minced and the soluble constituents extracted by cold water, pressure being applied to complete the separation of the fluid from

the insoluble fibres. The solution thus obtained is heated to the boiling-point to coagulate the albumen contained in it, and baryta-water is subsequently added to it as long as it continues to carry down any phosphoric acid.

After filtration, the liquid is evaporated in a water-bath, and the crystals first obtained are purified by animal charcoal.

Creatine crystallizes in clear prisms, which contain a molecule of water of crystallization. They require 74 parts of cold water to dissolve them. In absolute alcohol and in ether creatine is almost insoluble. It combines at temperatures below 30° with acids, forming salts, from which it can be recovered again. But when heated to a temperature above 30°, the creatine in one of these salts gradually loses water and passes over into creatinine—

$$\underbrace{C^4H^9N^3O^2}_{\text{Creatine.}} - H^2O = \underbrace{C^4H^7N^3O}_{\text{Creatinine.}}.$$

When heated with soda-lime creatine evolves methylamine. The same product is formed together with ammonia by the oxidizing action of nitric acid upon it. These reactions shew that the radical methyle is contained in the molecule of creatine. When boiled with baryta-water creatine takes up the elements of water, and decomposes into sarkosine and urea—

$$\underbrace{C^4H^9N^3O^2}_{\text{Creatine.}} + H^2O = \underbrace{C^3H^7NO^2}_{\text{Sarkosine.}} + CH^4N^2O.$$

And sarkosine is proved to be a methylated glycocoll ($C^2H^4(CH^3)NO^2$); for it has been made by the action of monochloracetic acid on methylamine—

$$C^2H^3ClO^2 + CH^3NH^2 = ClH + C^3H^7NO^2.$$

When an aqueous solution of creatine is boiled with mercuric oxide a compound called methyluramine, but which

might with advantage be termed methylated guanidin, is formed, together with oxalic acid—

$$C^4H^9N^3O^2 + O^2 = CH^4(CH^3)N^3 + C^2H^2O^4.$$

Some carbonic acid is given off at the same time.

**333.** Creatinine ($C^4H^7N^3O$) is found in the juice of flesh, and also in the human urine, as well as in the urine of horses and dogs, and especially in calves' urine.

It is also formed by the action of hot aqueous acids on creatine. To prepare it from urine, calcic chloride should be added in sufficient quantity to precipitate the phosphates, &c. from the liquid previously neutralized by lime water. The filtrate should be evaporated to crystallization, and the mother liquid from which the salts have been deposited should be mixed with a very strong solution of zinc chloride. Crystals containing creatinine combined with zinc chloride are deposited from this mixture after a few days' standing. These crystals can be dissolved in hot water and decomposed by plumbic oxide. The solution of creatinine is finally purified by animal charcoal.

Creatinine is much more soluble than creatine in water, for at 16°C it only requires 11.5 parts of water for its solution. It dissolves still more readily in hot water, and crystallizes from a hot saturated solution in needles. Its aqueous solution has an alkaline reaction to litmus-paper, and expels ammonia from its salts.

The platinum salt ($PtCl^6H^2(C^4H^7N^3O)^2$) is soluble. The compound with zinc chloride has a composition represented by the formula $ZnCl^2(C^3H^7N^3O)^2$. It is slightly soluble in water, and insoluble in alcohol.

Creatinine is converted into creatine by boiling with an aqueous alkali. Even plumbic oxide, in a boiling solution of creatinine, slowly produces the same change.

# CHAPTER LVI.

**334. Theine** ($C^8H^{10}N^4O^2$) and theobromine ($C^7H^8N^4O^2$) are bodies of great importance as aliments. Their transformations prove that they are nearly related to uric acid in constitution.

Theine is contained in tea, coffee, and in maté, or Paraguay tea, and also in a substance called guarana. It was called caffeine when first obtained from coffee, but its properties are in all respects the same, from whichever of the above-named vegetable bodies it may have been extracted.

Tea-leaves contain from two to four per cent. of theine; coffee-berries rather less than one per cent. Paraguay tea contains rather more than one per cent. of it. To prepare theine a cold alcoholic infusion of tea-leaves is precipitated by plumbic acetate, for the removal of the tannin which is present. The excess of lead is precipitated from the filtrate by sulphuretted hydrogen; the free acetic acid is neutralized by potash, and the liquid is evaporated to crystallization.

Theine crystallizes in long silky needles, which contain a molecule of water. It dissolves in water, alcohol, or ether. When gradually heated it sublimes without decomposition. It combines with acids, forming salts (such as the hydrochlorate $C^8H^{10}N^4O^2HCl$). Water decomposes this compound easily, and hydrochloric acid evaporates from it in warm air—so weak a base is the theine. The platinum salt $(PtCl^6H^2(C^8H^{10}N^4O^2)^2)$ is but slightly soluble in water, but the gold salt ($AuCl^4HC^8H^{10}N^4O^2$) is more soluble.

Oxidizing agents, such as nitric acid or chlorine, form in presence of water a compound called amalic acid, which is

alloxantin, in which four atoms of hydrogen are replaced by four atoms of methyle: thus, $C^8(CH^3)^4N^4O^7$. The further action of the same oxidizing agents forms cholestrophane, which is in constitution dimethyl-parabanic acid ($C^3(CH^3)^2N^2O^3$).

When acted upon by nitric acid and subsequently by ammonia, theine yields a purple-coloured product, similar to that obtained from uric acid. When boiled with potash theine is decomposed, with evolution of methylamine.

**335.** Theobromine ($C^7H^8N^4O^2$) is contained in chocolate, and is prepared from the cacao-nuts. It resembles theine in its chemical properties, and no doubt also in its action upon the human system.

An aqueous solution of theobromine mixed with ammonia is precipitated by argentic nitrate. The precipitate is a silver salt of the composition $C^7H^7AgN^4O^2$. By the action of methylic iodide upon this compound at 100°, Strecker has prepared theine—

$$C^7H^7AgN^4O^2 + CH^3I = C^7H^7CH^3N^4O^2 + AgI.$$

This reaction proves theine to be methylated theobromine.

But theobromine yields methylamine by the action of various destructive reagents, and must therefore be admitted to contain the radical methyle in its molecule. The body xanthin ($C^5H^4N^4O^2$), described above, differs from theobromine empirically by $(CH^2)^2$, and Strecker was led by this circumstance to prepare and examine dimethyle xanthin—

$$C^5H^2(CH^3)^2N^4O^2.$$

He found it to be isomeric, and not identical with theobromine.

From these facts it is inferred that theobromine is derived from a body of the composition $C^6H^6N^4O^2$, by the substitution of methyle for one atom of hydrogen—

$$(C^6H^5(CH^3)N^4O^2);$$

and that theine is similarly formed by the replacement of two

atoms of hydrogen in that same body by two atoms of methyle ($C^6 H^4 (C H^3)^2 N^4 O^2$).

**336.** In the bile of man, of oxen, sheep, pigs, and other animals, compounds analogous to soap in their properties and constitution have been discovered. Some remarkable transformations of the acids contained in these compounds have been explained by Strecker's able investigations, aided by the results of many previous investigations. Ox bile is the material most easily obtained in abundance for the preparation of these compounds. The liquid is usually of a brown colour, and must be used quite fresh, as it very soon undergoes putrefaction. The liquid is alkaline to test-paper from the presence of soda combined with the weak acids of the bile. Dry sodic sulphate dissolves in large quantities in bile, especially with the aid of heat, and if the liquid be saturated by this salt, the original salts of the bile are precipitated in the form of a brown resinous mass, very much in the same way as a soap is precipitated from aqueous solution by the action of salt.

The solid matter obtained in this way, or by evaporating the bile to dryness in a water-bath, should be treated with alcohol, which takes up the salts of the bile and the colouring matter, leaving mucus and some mineral salts undissolved. The addition of ether to the alcoholic solution of the salts of the bile causes a precipitate; and if the precipitation of a large quantity of the solution be effected in successive steps, and each successive precipitate kept separate, it is found that all the colouring matter is carried down by the first portions precipitated, and the later portions are colourless. By redissolving these colourless precipitates in alcohol, pouring ether onto the top of the solution, and leaving it in a closed flask, the salts of the bile can be obtained in crystals.

These crystals consist of the soda-salts of two acids which

have been called by Strecker cholic acid and taurocholic acid. Both of these acids contain carbon, hydrogen, nitrogen, and oxygen; but taurocholic acid contains sulphur in addition to those four elements. The proportion between these two acids varies in different sorts of bile, that from fishes being particularly rich in taurocholic acid. The name 'glycocholic' acid is applied by some chemists to Strecker's cholic acid, but the shorter name is preferable.

**337.** Sodic cholate ($C^{26}H^{42}NaNO^6$) and sodic taurocholate ($C^{26}H^{44}NaO^7S$) dissolve readily in water, and mineral acids precipitate their respective hydrogen salts.

Strong sulphuric acid added in excess dissolves the precipitate first formed in a solution of bile; and the addition of a strong syrup of cane-sugar to this hot mixture causes the appearance of a beautiful purple colour, which disappears on the subsequent addition of water. This reaction is known as Pettenkofer's test for the acids of the bile. It belongs also to cholalic acid.

Both cholic and taurocholic acids are decomposed by continued ebullition, in presence of an excess of baryta. Cholic acid takes up a molecule of water, and forms cholalic acid and glycocoll—

$$\underbrace{C^{26}H^{43}NO^6}_{\text{Cholic acid.}} + H^2O = \underbrace{C^{24}H^{40}O^5}_{\text{Cholalic acid.}} + \underbrace{C^2H^5NO^2}_{\text{Glycocoll.}}.$$

**338.** Taurocholic acid also yields cholalic acid, but the other product is taurine—

$$\underbrace{C^{26}H^{45}NSO^7}_{\text{Taurocholic acid.}} + H^2O = \underbrace{C^{24}H^{40}O^5}_{\text{Cholalic acid.}} + \underbrace{C^2H^7NO^3S}_{\text{Taurine.}}.$$

Taurine had been discovered for many years, and was represented by a formula containing no sulphur, but two atoms of oxygen instead of one of sulphur. Strecker has

shewn that it is the amide of isethionic acid, an acid formed by the combination of olefiant gas with anhydrous sulphuric acid—

$$\underbrace{C^2H^5(NH^4)SO^4}_{\text{Ammonia isethionate.}} - H^2O = \underbrace{C^2H^7NSO^3}_{\text{Taurine.}}.$$

The bile of hogs contains in place of cholic acid an acid homologous with it, which Strecker has named, from its source, hyocholic acid. Hyocholic acid is decomposed like cholic acid, by boiling with alkalies, and instead of cholalic acid it yields an acid containing $CH^2$ in addition to the elements of cholalic acid, and called hyocholalic acid.

Cholesterine ($C^{26}H^{44}O$) is a beautiful crystalline body, which has been usually classed among fats, but which more recent investigations have proved to possess an alcoholic constitution. It combines with stearic or benzoic acid like a monatomic alcohol.

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# CHAPTER LVII.

**339.** One of the most important groups of organic compounds are the so-called alkaloids; organic bases possessing powerful medicinal properties, and very complex molecules of which the arrangements are for the most part unknown to us.

The most valuable alkaloid of cinchona bark is

**Chinine** ($C^{20}H^{24}N^2O^2$). The bark contains this base together with cinchonine, combined with chinic acid.

For the preparation of chinine the bark is ground and

boiled with dilute sulphuric or hydrochloric acid. The strained liquid is precipitated by sodic carbonate, and the precipitate, consisting of chinine and cinchonine, is dissolved in dilute sulphuric acid and crystallized, the chinine salt being first deposited. If the mixed bases be dissolved in spirits of wine, after precipitation of the original extract and desiccation of the precipitate, the cinchonine can in great part be crystallized out from the alcoholic solution, while the chinine remains in the mother liquid.

Chinine is slightly soluble in water, but it dissolves readily in alcohol or in ether. It forms crystallizable salts, of which an aqueous solution has an intensely bitter taste.

Solutions of salts of chinine, containing free acid, are exceedingly fluorescent. In light containing ultraviolet rays an acid solution of the sulphate presents on its surface a beautiful blue opalescent appearance.

Ammonia and potash precipitate chinine from an aqueous solution of one of its salts, and the precipitate is scarcely at all soluble in an excess of the precipitant.

Chlorine water acts on a solution of the sulphate in such a manner that the subsequent addition of ammonia forms a deep emerald green solution.

Chinine combines with hydrochloric acid in two proportions, forming the compounds

$$C^{20}H^{24}N^2O^2HCl \text{ and } C^{20}H^{24}N^2O^2(HCl)^2.$$

Its platinum salt corresponds to the latter of these compounds, for it contains its elements in the following proportions—$PtCl^6H^2C^{20}H^{24}N^2O^2$. It is but slightly soluble in water.

There are two chinine sulphates. That which usually occurs in commerce has a composition represented by the formula $SO^4H^2(C^{20}H^{24}N^2O^2)^2(H^2O)^7$. It consists of needle-shaped crystals, which dissolve very slightly in water. The crystals are gradually decomposed, and become brown,

by exposure to sunshine. Dilute sulphuric acid dissolves these crystals readily, forming the compound

$$SO^4H^2C^{20}H^{24}N^2O^2(H^2O)^7.$$

When this salt is dissolved in strong acetic acid, and an alcoholic solution of iodine is gradually added to it, a compound is formed which crystallizes out from the solution in flat plates. These plates are called the sulphate of iodochinine, and are represented by the formula

$$SO^4H^2C^{20}H^{24}N^2O^2I^2(H^2O)^5.$$

They exhibit a green colour by reflected light, and are particularly interesting from the polarizing action which they exert upon transmitted light.

Chinine sulphate has in solution a powerful levorotatory action on polarized light. When heated to 100°C the salt is phosphorescent.

The commercial salt sometimes contains cinchonine, and this admixture can be discovered by adding ammonia in slight excess to a concentrated solution of the acid sulphate and then agitating the mixture with ether. Cinchonine remains undissolved.

There are two alkaloids isomeric with chinine, and formed from it. These bases are called chinidine and chinicine. They are obtained from a resinous substance called quinoidine.

**340. Cinchonine** ($C^{20}H^{24}N^2O$) crystallizes from an alcoholic solution in the form of needles. Its solution has an alkaline reaction to test-paper. In cold water it is almost insoluble, and in boiling water very slightly soluble. The alkaloid melts at 105°, and can be partially sublimed. Its salts exert a powerful dextrorotatory action on light. They do not give a green product when treated by chlorine and subsequently by ammonia.

There are two hydrochlorates ($C^{20}H^{24}N^2OHCl$ and $C^{20}H^{24}N^2O(HCl)^2$). The platinum salt is represented by

the formula $C^{20}H^{24}N^2OPtCl^6H^2$. There are two sulphates, viz.—

$SO^4H^2(C^{20}H^{24}N^2O)^2$ and $SO^4H^2C^{20}H^{24}N^2O$.

Both chinine and cinchonine are decomposed by fusion with potash, yielding an oily product of alkaline properties, called quinoleine.

Both alkaloids unite with methylic iodide or ethylic iodide, forming the compounds—

$C^{20}H^{24}N^2O^2CH^3I$ and $C^{20}H^{24}N^2OCH^3I$.

The methyle thus added to the composition of the base is not in the place of any typical hydrogen of ammonia, but in the place of the fourth atom of hydrogen which is added to an ammonia when an ammonium salt is formed. Freshly-precipitated argentic hydrate, added to the solution of one of these iodides, removes the iodine and replaces it by HO—

$$C^{20}H^{24}N^2O^2CH^3I + HOAg = C^{20}H^{24}N^2O^2CH^3HO + AgI.$$

The hydrates thus obtained are very strong bases.

**341.** **Opium** is the name given to a mixture of a number of alkaloids with resins, mucilage, caoutchouc, &c., and a peculiar acid called meconic acid. The substance is obtained by scratching unripe poppy capsules, and collecting, after it has dried, the milky juice which exudes. The opium undergoes a process of fermentation before it is exported for use. The proportions in which the various constituents are present vary in different specimens of opium. The best varieties, such as Smyrna opium, sometimes contain as much as fifteen per cent. of morphia, while the inferior sorts sometimes contain as little as three per cent. of morphia, or even less. Narcotine and meconic acid are present in quantities varying from six to eight per cent., and codeia, thebaia, papaverine, opianine, narceia, and meconine are present in far smaller quantities.

**342.** **Morphia** ($C^{17}H^{19}NO^3$) is usually prepared by

dissolving in water the soluble constituents of the opium, neutralizing the solution by chalk, and adding calcic chloride in quantity sufficient for the precipitation of the meconic acid. The alkaloids are thus left in solution combined with hydrochloric acid, and are filtered off from the precipitate of calcic meconate, and evaporated to crystallization. The morphia hydrochlorate crystallizes out first, while the mother liquid retains a quantity of colouring matter with a little morphia and other bases. A second crystallization yields a mixture of the hydrochlorates of codeia and morphia. Morphia can be precipitated with facility by ammonia from a solution of its hydrochlorate.

Another method of preparing morphia from opium consists in boiling the aqueous extract of the drug with milk of lime, and filtering off the alkaline solution thus obtained from the undissolved matter. The morphia is combined with lime in the solution, and can be precipitated from it by the action of sal ammonia with the aid of heat. Ammonia evaporates, while morphia falls down and calcic chloride remains in solution.

Morphia requires about 1000 times its weight of cold water for its solution, and about 400 times its weight of boiling water. The solution has an alkaline reaction to turmeric paper. Morphia dissolves readily in alcohol, but is insoluble in ether and in chloroform.

The alkaloid is readily oxidized by iodic acid or by ferric salts. Neutral ferric chloride forms with morphia a dark blue compound not very unlike ink, and this property serves as a test for morphia. Although readily soluble in fixed alkalies, morphia is but slightly soluble in ammonia.

Morphia hydrochlorate ($C^{17}H^{19}NO^3HCl(H^2O)^3$) dissolves in sixteen parts of cold water, or in one part of boiling water. Its platinum salt is represented by the formula

$$(C^{17}H^{19}NO^3)^2PtCl^6H^2.$$

Narcotine ($C^{22}H^{23}NO^7$) is a much weaker base than morphia, as might be inferred from the larger quantity of oxygen contained in it. It is readily soluble in ether or chloroform, and can thus be separated from morphia. Narcotine is readily oxidizable, and undergoes numerous interesting decompositions, which have been ably investigated by Matthiessen and Foster. When acted on by hydriodic acid in aqueous solution a molecule of narcotine forms three molecules of methylic iodide.

**343.** The chief alkaloids of the Strychnos tribe of plants are **Strychnia** and **Brucia.**

These alkaloids can be prepared from the nux vomica, by rasping the seeds and boiling them with alcohol containing one or two per cent. of sulphuric acid. The solution thus obtained is neutralized by lime, and the alcoholic solution of the two alkaloids is evaporated to dryness. The alkaloids are subsequently dissolved in dilute nitric acid, and separated by crystallization of their nitrates, the strychnia nitrate being less soluble than brucia nitrate.

Strychnia ($C^{21}H^{22}N^2O^2$) is easily precipitated by ammonia or potash from a solution of one of its salts, and is not soluble in an excess of potash. It is almost insoluble in water, or in absolutely dry alcohol. The very small quantity of it which dissolves in water is, however, sufficient to impart a bitter taste to the liquid. Animal charcoal removes strychnia from an aqueous solution. It is readily soluble in spirits of wine, and it dissolves also in chloroform, but not in ether. Strychnia is not reddened by the action of strong nitric acid, and its freedom from brucia is thus tested.

When mixed with plumbic peroxide, and then moistened by strong sulphuric acid, strychnia forms a blue compound, which soon changes to a violet one, and ultimately becomes red and brown. This colour-test is used for the detection of strychnia.

The platinum salt of strychnia is almost insoluble in water. It is represented by the formula

$$Pt\,Cl^6H^2(C^{21}H^{22}N^2O^2)^2.$$

There is a normal sulphate of the composition

$$SO^4H^2(C^{21}H^{22}N^2O^2)^2,$$

and an acid salt, $SO^4H^2C^{21}H^{22}N^2O^2$.

Strychnia and its salts produce lockjaw, or 'tetanus,' and the alkaloid can be detected by its action on a frog, even when given in an exceedingly minute quantity.

Brucia ($C^{23}H^{26}N^2O^4$) is soluble in about 850 parts of boiling water, and in a far smaller quantity of spirits of wine. It forms large crystals containing four molecules of water. For the preparation of the pure alkaloid its oxalate is washed with dry alcohol at 0°C. The salt is then dissolved in water, decomposed by lime, evaporated to dryness, and then crystallized from alcohol.

Strong nitric acid in contact produces a deep red colour with brucia, whilst methylic nitrite is evolved.

**344. Nicotine** ($C^{10}H^{14}N^2$) is a volatile and liquid alkaloid contained in tobacco, and imparting to that plant the narcotic properties for which its leaves are used. Nicotine is a very strong base, belonging to the class of tertiary diamines. It boils at about 250°, is readily soluble in water, and forms crystallizable salts. Its hydrochlorate is represented by the formula $C^{10}H^{14}N^2Cl^2H^2$.

Nicotine is exceedingly poisonous; five milligrammes of it placed on the tongue of a middle-sized dog having been found sufficient to kill the animal in three minutes.

# CHAPTER LVIII.

**345.** Amongst organic compounds of which the molecular arrangement is but little known there are two important colouring bodies which deserve some study, viz. indigo and alizarine.

**Indigo** ($C^8H^5NO$) is manufactured in India by macerating the indigo plants with water in large vats. A process of fermentation takes place, by which indigo-white is formed and dissolved by the water. As soon as the process is judged to be complete, the water is pressed out from the plants and led into vats, in which air has access to it, and precipitates indigo-blue from the solution. The process is aided by beating the surface of the liquid with flat shovels, whereby more of the liquid is brought into contact with air, and the precipitate is rendered more dense.

The indigo-blue which is collected in this manner contains various earthy and other impurities, sometimes in large quantity. Good specimens contain 50 to 60 per cent. of indigo, besides substances called indigo-gluten, indigo-red, indigo-brown, and other resinous bodies. Some of these foreign bodies can be dissolved out by the successive action of dilute sulphuric acid, boiling water, and alcohol; but the indigo-vat affords the best means of purifying the colouring-matter. There are various sorts of so-called indigo-vat, but the operation in all of them consists in transforming the indigo-blue, by the action of a reducing agent, into indigo-white, and dissolving this indigo-white. Water with lime and ferrous sulphate is a mixture which forms a 'vat' of frequent use. The ferrous oxide becomes converted into

ferric oxide, whilst the indigo is reduced and dissolved. Air should be excluded during the operation.

From the solution formed in the vat indigo-white can be precipitated by hydrochloric acid; or indigo-blue by the absorption of oxygen from the air.

**Indigo-blue** ($C^8H^5NO$) is a neutral solid, presenting a coppery lustre by reflected light. When heated it melts, and a small quantity can be sublimed in the form of crystals. Several oxidizing agents—such as chromic acid—are capable of converting indigo into isatine ($C^8H^5NO^2$). By further oxidation by strong nitric acid this is in its turn converted into

Nitrosalycylic acid ($C^7H^5(NO^2)O^3$), and ultimately into carbazotic acid ($C^6H^3(NO^2)^3O$).

Indigo is decomposed by strong aqueous potash, with the aid of heat, forming, according to Gerhardt, a product of oxidation, isatic acid; and by simultaneous reduction of another portion, indigo-white—

$$(C^8H^5NO)^2 + H^2KO^2 = \underbrace{C^8H^6KNO^3}_{\text{Potassic isatate.}} + \underbrace{C^{16}H^{12}N^2O^2}_{\text{Indigo-white.}}$$

When melted with potash it evolves hydrogen, and potassic anthranilate ($C^6H^5KNO^2$) is formed. When distilled with potash indigo yields aniline.

**346. Alizarine** ($C^{10}H^6O^3$) is a valuable dye obtained from madder-root. Some alizarine is found ready formed in the roots, but more of it is obtained by the decomposition of a yellowish compound which is present in the root. This yellowish compound can be extracted by cold water (alizarine is not soluble in it), and the solution can be used for dyeing with alizarine colours. Alizarine dissolves in alkalies, or alkaline carbonates, forming purple solutions, from which it is precipitated on the addition of an acid.

It dissolves in alcohol or ether, and also in strong sul-

phuric acid, from which it is thrown down again by water. By ebullition with nitric acid it is oxidized, forming naphthalic and oxalic acids—

$$\underbrace{C^{10}H^6O^3}_{\text{Alizarine.}} + H^2O + O^4 = \underbrace{C^8H^6O^4}_{\text{Naphthalic acid.}} + C^2H^2O^4.$$

Alizarine crystallizes in red prisms, which can be volatilized at 215°.

**347. Orceine** ($C^7H^7NO^3$) is a red colouring-matter which is present in litmus. It is made by exposing orcine to the simultaneous action of ammonia and air—

$$\underbrace{C^7H^8O^2}_{\text{Orcine.}} + NH^3 + O^3 = \underbrace{C^7H^7NO^3}_{\text{Orceine.}} + (H^2O)^2.$$

Orceine is very slightly soluble in water or ether, but alcohol dissolves it readily. It dissolves in aqueous potash or ammonia.

**Orcine** ($C^7H^8O^2$) is made by boiling a suitable lichen with milk of lime for several hours. The liquid is filtered, deprived of the lime in it by oxalic acid, and reduced to a small bulk. The orcine is dissolved in alcohol, and crystallized from that solution, and subsequently from solution in ether.

Orcine crystallizes with a molecule of water, which is given off at 100°. At a high temperature it can be sublimed without decomposition.

The formation of the orcine is due to the decomposition of erithrine contained in the lichens. The reaction gives rise to the formation of orsellic acid and erithrite—

$$\underbrace{C^{20}H^{22}O^{10}}_{\text{Erithrine.}} + (H^2O)^2 = \underbrace{(C^8H^8O^4)^2}_{\text{Orsellic acid.}} + \underbrace{C^4H^{10}O^4}_{\text{Erithrite.}}.$$

Orsellic acid breaks up subsequently into carbonic acid and orcine.

**348. Turpentine** ($C^{10}H^{16}$) is a member of a very numerous family of hydrocarbons which occur in plants, and often impart to them their peculiar smell. They are classed among essential oils; of which several (such as gaultheria oil, oil of cinnamon, &c.) have already been described. Many plants supply hydrocarbons isomeric with oil of turpentine. Among the most important of these isomeric hydrocarbons may be mentioned oil of lemons, oil of bergamott, oil of birch, oil of camomile, oil of carraway, oil of juniper, oil of ginger, oil of hops, oil of parsley, oil of pepper, and oil of thyme.

These essential oils are frequently prepared by distilling the plants or parts of plants containing them, with water. The oils are carried over into a receiver by the steam, at a temperature far below their own boiling-points. Many of them are, however, altered by exposure to the temperature of 100°, and deteriorated as perfumes. These are accordingly collected at the atmospheric temperature by placing a considerable surface of some inodorous fat in a suitable box near to the flowers which are exhaling the fragrant oil. The fat absorbs and dissolves it with its original properties.

Commercial turpentine varies considerably in its properties, according to the plant from which it was collected; but in addition to a hydrocarbon of the composition $C^{10}H^{16}$ it always contains a resinous body formed by the oxidation of that hydrocarbon. It is usually purified by rectification, the resin being left in the still. Its specific gravity is about 0.86, and it boils at 160°. Some varieties of it are dextrorotatory, some levorotatory.

It dissolves sulphur or phosphorus. It is also a good solvent for grease.

It is almost insoluble in water, but dissolves in alcohol or ether. It absorbs oxygen rapidly from the air, especially when mixed with litharge or ceruse.

It combines with hydrochloric acid, forming crystalline compounds. It also combines with water under favourable circumstances, forming crystalline hydrates.

These compounds are sometimes called artificial camphors.

Turpentine is readily oxidized by nitric acid, forming terebic acid, oxalic acid, and resinous bodies.

**349. Camphor** ($C^{10}H^{16}O$) is the common camphor of commerce. It is made from a laurel tree, and is often called laurel camphor. It has a density of 0.996, and it boils at 204°. It dissolves to a very small extent in water, and undergoes during the process of solution a rotatory motion. In alcohol or ether it is readily soluble, also in fixed and volatile oils.

When heated under pressure with potassic hydrate it unites with the alkali, forming a campholate—

$$C^{10}H^{16}O + HKO = C^{10}H^{17}KO^2.$$

Anhydrous phosphoric acid deprives it of water, liberating a hydrocarbon called cymene, or, by some authors, cymol—

$$C^{10}H^{16}O - H^2O = C^{10}H^{14}.$$

When boiled with strong nitric acid camphor is oxidized, forming camphoric acid—

$$C^{10}H^{16}O + O^3 = C^{10}H^{16}O^4.$$

Borneo camphor ($C^{10}H^{18}O$) is another compound which is sometimes found in commerce. It is deprived of two atoms of hydrogen by the action of nitric acid, and converted into laurel camphor. Anhydrous phosphoric acid liberates from it a hydrocarbon isomeric with turpentine.

## TABLE I.

*Units of heat evolved by complete oxidation of one gramme of*

| | | | |
|---|---|---|---|
| Hydrogen | 34462° | Zinc | 1330 |
| Charcoal | 8080° | Iron (forming $Fe^3O^2$) | 1582° |
| Carbonic oxide | 2403° | Tin | 1147 |
| Sulphur (forming $So^2$) | 2220° | Copper | 603 |
| Phosphorus | 5747 | | |

## TABLE II.

*Specific gravity, at* 14°C, *of ammonia solutions of various strengths, from Carius' determinations.*

| Sp. gr. | Percent. of ammonia. | Sp. gr. | Percent. of ammonia. | Sp. gr. | Percent. of ammonia. |
|---|---|---|---|---|---|
| 0.8844 | 36.0 | 0.9191 | 22.0 | 0.9556 | 10.0 |
| 0.8885 | 34.0 | 0.9251 | 20.0 | 0.9670 | 8.0 |
| 0.8929 | 32.0 | 0.9314 | 18.0 | 0.9749 | 6.0 |
| 0.8953 | 30.0 | 0.9380 | 16.0 | 0.9831 | 4.0 |
| 0.9026 | 28.0 | 0.9449 | 14.0 | 0.9915 | 2.0 |
| 0.9078 | 26.0 | 0.9520 | 12.0 | 0.9959 | 1.0 |
| 0.9133 | 24.0 | | | | |

## TABLE III.

*Percentage of sulphuric acid in hydrates of various densities at* 15.5°. (URE.)

| Sp. gr. | Percent. of $SO^3$. | Sp. gr. | Percent. of $SO^3$. | Sp. gr. | Percent. of $SO^3$. |
|---|---|---|---|---|---|
| 1.8460 | 81.54 | 1.6624 | 61.97 | 1.4265 | 44.03 |
| 1.8415 | 79.90 | 1.6415 | 60.34 | 1.4073 | 42.40 |
| 1.8366 | 78.28 | 1.6204 | 58.71 | 1.3884 | 40.77 |
| 1.8288 | 76.65 | 1.5957 | 57.08 | 1.3697 | 39.14 |
| 1.8181 | 75.02 | 1.5760 | 55.45 | 1.3530 | 37.51 |
| 1.8070 | 73.39 | 1.5503 | 53.82 | 1.3345 | 35.88 |
| 1.7901 | 71.75 | 1.5280 | 52.18 | 1.3165 | 34.25 |
| 1.7728 | 70.12 | 1.5066 | 50.55 | 1.2999 | 32.61 |
| 1.7540 | 68.49 | 1.4860 | 48.92 | 1.2826 | 30.98 |
| 1.7315 | 66.86 | 1.4660 | 47.29 | 1.2654 | 29.35 |
| 1.7080 | 65.23 | 1.4460 | 45.66 | 1.2490 | 27.22 |
| 1.6860 | 63.60 | | | | |

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# ERRATA.

Page 64, line 7, *for* $HG^n$ *read* $Hg^n$.

„ 187, line 5, *for* in *read* on.

„ 187, middle of page (twice), *for* $Fe^2O^3H^6$ *read* $Fe^2O^6H^6$.

„ 188, middle, *for* ferrycyanide *read* ferricyanide.

„ 189, line 15, *after* acid *insert* contained in the salt.

„ 191, § 182, line 2, *for* in *read* on.

„ 196, line 1, *for* Cromium *read* Chromium.

„ 205, four from bottom, *after* washed *insert* and roasted frequently.

„ 238, line 7, *for* $Po^4Li^3$ *read* $PO^4Li^3$.

„ 242, middle, *omit* its atom.

„ 244, line 9, *for* empyrical *read* empirical.

„ 248–9, passim, *for* infusoriæ *read* infusoria.

„ 281, middle, *for* terms *read* bodies.

„ 289, line 7, *for* ethylic iodide *read* methylic iodide.

„ 290, lines 3–4, *for* $Po^4$ and $Po^3$ *read* $PO^4$ and $PO^3$.

„ 313, middle, *for* $\begin{matrix}O^2\\H\end{matrix}\begin{matrix}HCl^2O\\\end{matrix}O$ *read* $\begin{matrix}C^2\\H\end{matrix}\begin{matrix}HCl^2O\\\end{matrix}O$.

„ 314, *for* Butyric acid (small) *read* **Butyric Acid** (large), and new paragraph.

„ 331, line 5, *for* $\left.\begin{matrix}C^2(CH^3)\\H\end{matrix}\begin{matrix}(C^2H^5)O\\\end{matrix}\right\}O^2$ *read* $\left.\begin{matrix}C^2(CH^3)\\H^2\end{matrix}\begin{matrix}(C^2H^7)O\\\end{matrix}\right\}O^2$.

„ 333, line 7 from bottom, *for* acid *read* chloride.

„ 344, line 7, *for* *tri*atomic *read* *tetra*tomic.

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